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Graphitelike Layers in Coals and High Vacuum Distillation Products

S. ERGUN

X-Ray scattering intensities have been obtained of a vitrinite component of a bituminous coal and of the distillate and residues prepared from it by high vacuum distillation. Comparison of their intensities at high and moderately low angles indicated that both the distillate and residues contained aromatic layers. Scattering intensities of the distillate and of the residue obtained after 10 per cent weight loss were similar and more diffuse than those of the original vitrinite. The results of intensity profile analyses indicated that, in the vitrinite examined (36 per cent volatile matter), appreciable quantities of peripheral groups were not present and that the planar aromatic nuclei were small, consisting of one to three rings. The present findings can be tentatively explained if the vitrinite is conceived as a polymer of small, partially oriented planar units which depolymerize upon heating; some of the structural entities are set free as vapour, others recombine to form a highly disordered carbon skeleton.

VARIOUS investigators have examined coals, cokes and other carbonaceous materials by means of X-rays. Scattered intensity curves have been interpreted[1] in terms of condensed aromatic (graphite-like) layers varying in size from 7 to 16 Å. The existence of small aromatic layers was also supported by Fourier integral analysis of the scattered intensities[2]. However, X-rays and other physical and chemical evidence indicates that not all of the carbon atoms are part of the aromatic rings; the non-aromatic carbon atoms are regarded as roentgenamorphous by X-ray workers.

Coals undergo a loss of weight upon heating; the material lost is called volatile matter. Generally, the volatile matter yield of coals increases with an increase in their hydrogen and oxygen content. X-Ray patterns of coals containing the larger amounts of volatile matter are more diffuse and have been explained on the basis of higher roentgenamorphous carbon content. These observations suggest the association of amorphous carbon, hydrogen and oxygen with the volatile matter. However, physicochemical properties of condensable volatile matter are believed to show a close structural relationship to the raw coal, suggesting that some aromatic clusters are set free during devolatilization. Therefore, it appeared that an X-ray study of high vacuum distillation products of coal might lead to a better understanding of devolatilization and consequently of the basic structure of coal.

EXPERIMENTAL PROCEDURE

The vitrinite component of a high volatile bituminous coal (Pittsburgh bed) was used in the present study. The vitrinite was selected from a column sample and crushed in a mortar to pass through 40-mesh. The crushed particles were examined under a microscope, and the visible mineral matter and other petrographic components were removed. The resulting sample contained about 0·5 per cent ash, as determined by chemical analysis.

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Distillations were carried out in a vacuum still. The still had a flat cold surface directly above the hot plate to collect the condensable distillate; the space between the two plates was narrow. A 10 g sample of 40 to 60 mesh vitrinite was placed in the annular grooves of the hot plate. The sample was heated rapidly to 350°C, then slowly at a rate of 3°C per minute until a predetermined temperature was reached. This temperature was maintained until a desired weight loss occurred, as judged from prior experience. A vacuum of about 10^{-3} mm of mercury was maintained during heating. One

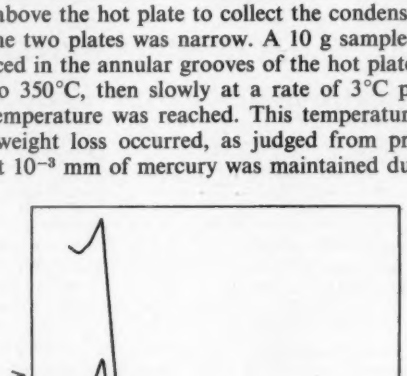

Figure 1. X-Ray scattering intensities of a vitrinite and its high vacuum distillation products

sample was heated to 450°C and distilled to about 10 per cent loss in weight, another to 510°C to result in a 20 per cent weight loss. Portions of the distillates and residues collected were placed in vials and kept under helium until X-ray examination.

X-Ray scattering intensities were obtained from extruded cylindrical samples in an evacuated Debye–Scherrer camera. Monochromatic Cu K_α radiation was used. Exposures of about 90 hours were required. The films were developed and scattering intensities in arbitrary units were obtained with a densitometer. The intensities were then corrected for polarization and converted into electron units by the method of R. DIAMOND[3]. The resulting intensity curves for the vitrinite and its distillate and two residues are shown in *Figure 1*.

RESULTS AND DISCUSSION

From *Figure 1* it is seen that the scattering intensities of the distillate are not

those of amorphous material. The distillate has the diffuse intensity bands exhibited by vitrinites, i.e. the three major peaks generally interpreted as belonging to the (00*l*) and (*hk*) reflections of planar aromatic ring clusters. There are dissimilarities in the intensity curves of the vitrinite and its distillate, signifying differences in the structure. For example, the distillate has a shoulder on the (002) band (the first peak from the left) at a spacing of about 4 to 5 Å, where hydrogen-rich exinite components of coals exhibit a peak[4,5] generally referred to as the gamma band. These dissimilarities, however, are to be expected; the distillate melted at 40°C and contained about 7·5 per cent hydrogen as compared with 5·5 per cent for the vitrinite. An infra-red (i.r.) examination of a vacuum distillate of the same coal had led A. A. ORNING and B. GREIFER[6] to observe that the distillate retained the molecular configuration of coal as judged by comparing the spectra. Their observation and the present study support the suggestion that a substantial portion of the aromatic structures in coal is set free upon heating[7,8] rather than the contention that heating results in simply driving away peripheral groups that are attached to aromatic nuclei[3, 9–13].

From *Figure 1* it is seen that a 10 per cent loss in the weight of the vitrinite yielded a residue that scattered x-rays more diffusely than the original vitrinite. After a 20 per cent loss in weight, the (11) band (the third peak from the left) remained still more diffuse than that of the vitrinite. Earlier x-ray studies of carbonized coals[3, 12, 14] had shown an initial sharpening of the (002) band with increase in carbonization temperature up to about 500°C, followed by a reversal, i.e. becoming diffuse, to 700°C; further increase in carbonization temperature sharpened the peak again. The progressive sharpening was explained by parallel orientation of aromatic nuclei freed from side chains as a result of thermal destruction of peripheral groups; the increase in diffuseness was explained by an opposing reaction, i.e. interaction or recombination of side radicals of freed aromatic nuclei. The above workers had also observed a progressive sharpening of the (10) and (11) peaks (the second and third peaks from the left, respectively, in *Figure 1*) with carbonization temperature, the sharpening being gradual initially but more rapid at about 500°C. The sharpening was explained on the basis of destruction of peripheral groups that constitute roentgenamorphous material and growth or coalescence of freed aromatic ring clusters. However, the increased broadening of the (10) and (11) peaks of the residues observed in the present study is not in accordance with the concepts reviewed above, even though it is recognized here that the mode of temperature treatment would influence the properties of the products.

Figure 1 also shows that there is a greater similarity between the scattering intensities of the distillate and the 10 per cent residue than between those of the vitrinite and the distillate or residue. This similarity is further illustrated in *Figure 2*.

To obtain additional information about the ultrafine structure of vitrinite and its distillation products, the scattered intensities shown in *Figure 1* were analysed quantitatively by the method of DIAMOND[3, 15]. The results are shown in *Table 1*. The procedure involved a profile analysis of the major portion of the (11) peak, i.e. from $s = 0{\cdot}66$ to $0{\cdot}96$, in terms of roentgenamorphous

material and aromatic ring clusters of different sizes, i.e. 5·8, 8·4, 10, 15 and 20 Å. The vitrinite was found to contain 37 per cent roentgenamorphous material and the average size of the ring clusters was 7·6 Å (3 to 5 rings). The pattern of the distillate and of the residue of 10 and 20 per cent distillations indicated, respectively, 10, 7 and 13 per cent contents of amorphous

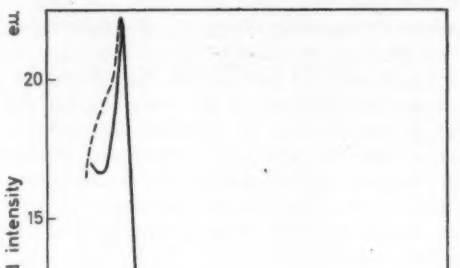

Figure 2. X-Ray scattering intensities of the distillate and residue after 10 per cent weight loss

material and the average sizes of the ring clusters were about 5·8 Å, i.e. 1 to 3 rings, with a slightly larger result, 6 Å, being obtained for the 20 per cent distillation residue.

The theoretical curves computed from the above analyses differed markedly from the observed curves outside the fitted range. This discrepancy may be

Table 1. Distribution of carbon in a vitrinite and its high vacuum distillation products

Material	*Atomic per cent in*			
	Roentgen-amorphous carbon	*Size group 1* 5·8 Å *(1–3 rings)*	*Size group 3* 8·4 Å *(5–7 rings)*	*Size group 5* 10 Å *(9–10 rings)*
Vitrinite	37	27	24	12
Distillate	10	90	—	—
Residue 1 (10% *weight loss*)	7	93	—	—
Residue 2 (20% *weight loss*)	13	78	9	—

attributed to a simplifying assumption involved in the above method that carbon atoms in coals or coal derivatives are either in aromatic ring clusters or are distributed randomly, i.e. gas-like scatterers. It appears that there are arrangements of non-aromatic carbons that lead to some diffuse X-ray interference pattern affecting the curves shown in *Figure 1*. Additional physical and chemical data and theoretical work on X-ray scattering from different arrangements of carbon and oxygen are needed.

Increased diffuseness of the (*hk*) reflections of the residue makes it doubtful that appreciable quantities of peripheral groups are present in the vitrinite. A reduction in the average layer size from 7·0 Å (3 to 5 rings) to about 5·8 Å (1 to 3 rings) upon a weight loss of only 10 per cent suggests that condensed aromatic nuclei larger than those found in the residue may not be present in the vitrinite. The fact that layer groups in the distillate were about the same size as those in the residue supports this suggestion. Larger groups obtained for the original vitrinite may be attributed to coplanar coalescence of smaller nuclei as a result of long-term pressure-induced orientation and packing. The X-ray[1] and optical[16] anisotropy of coals and the increase of anisotropy with unidirectional compression[17] have been explained on the basis of pressure-induced orientation. Thermal disturbance of orientation would affect the parallel as well as coplanar ordering of the layers. The increased diffuseness of the (002) band of the 10 per cent distillation residue is in keeping with this argument.

If the vitrinite examined is composed of small ring clusters (1 to 3 rings), stoichiometric considerations also would preclude the existence of peripheral groups in quantities sufficient to account for the volatile matter yield, 36 per cent. Therefore, devolatilization cannot be regarded as simply the removal of peripheral groups.

A comprehensive interpretation concerning the ultrafine structure of the vitrinite examined and the nature of the changes taking place during vacuum distillation is not possible at present. However, results of this study can be tentatively explained if the vitrinite is conceived as a polymer of small planar units, partially oriented under the influence of pressure. Upon thermal treatment, the orientation would be disturbed and depolymerization and cracking would occur, accompanied by several simultaneous and consecutive chemical reactions, such as hydrogenation, dehydrogenation, dealkylation, oxygen splitting, free radical formation, etc. Some of the structural entities would be set free as vapour; others would combine, probably as a result of interactions of side radicals, giving rise to a highly disordered carbon skeleton.

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Studies in Bomb Calorimetry IX— Formation of Sulphuric Acid

R. A. MOTT and C. PARKER

It has been found that the sulphur trioxide formed in the combustion of a solid fuel dissolves to a negligible extent in the water added to the bomb before a determination of calorific value, 85 per cent of the sulphur in coal and 95 per cent of the sulphur in coke being found in the water released or produced during the combustion of the fuel and deposited as fine droplets on the walls and cap of the bomb. The concentration of sulphuric acid in such droplets increases with increase in the sulphur content of the fuel and with decrease in its hydrogen and moisture contents. It is advised that the bomb should be washed out as soon as possible after the determination. For cokes of high sulphur (over 1·75 per cent) and low hydrogen contents, the addition of 0·05 g water to the sample is advised. Some of the sulphur trioxide reacts with the alumina pad which is used for coke and some remains in the gaseous phase. Thus, when using an independently determined sulphur content (S per cent) to make the sulphur correction the sulphuric acid in the bomb washings must be calculated from an 'effective' sulphur content (0·8 S—0·06 per cent) when computing the nitrogen correction from the total acidity. The validity of the 'sulphur correction' depends upon the assumption that the concentration of the sulphuric acid is between 5 and 15 per cent by weight. This assumption is valid for coals, except for very high (over 5) sulphur percentages, and for cokes unless they have an unusual combination of high sulphur (over 1·75) and low hydrogen percentages. For coke, when determining the sulphur correction from the bomb washings, the crucible residue must be added to the washings and the titration for total acidity carried out with barium hydroxide solution.

IN the determination of the gross calorific value of a solid fuel at constant volume by combustion with oxygen, under pressure, in a calorimetric bomb, sulphur dioxide is formed from the sulphur contained in fuel. In the presence of nitrogen peroxide (the nitrogen being derived from the air present in the bomb before filling with oxygen, or from the fuel, or both) the sulphur dioxide is oxidized to trioxide, which reacts with water droplets to form sulphuric acid. It is necessary to make an allowance for the heat evolved in these reactions: this allowance, known as the 'sulphur correction' (see Part IV of this series[1]), is usually taken to be 2·26 cal/mg of sulphur. As will be shown later, this is strictly valid only for an acid concentration within a particular range. Furthermore, it has been customary to assume (as in Part VI of this series[2]) that the acid concentration is uniform throughout the bomb, but it is now known that this is not so. This paper is concerned with an investigation of these two (related) topics.

Sulphur trioxide is not the only soluble gas formed by combustion of the fuel. Other such gases are carbon dioxide, nitrogen peroxide (necessitating the 'nitrogen correction') and hydrogen chloride (if the fuel contains chlorine). The water in which these gases dissolve comes from two sources. In the determination of both the effective heat capacity of the calorimeter and the calorific value of a fuel, 1 ml of water is placed in the bomb cup before charging the bomb with fuel and oxygen. The quantity of water required to saturate

the gas space is only of the order of 0·01 g, so that substantially all of the original 1 ml is available for solution of soluble gas produced by the combustion of the sample. In addition, some quantity of water is produced by the combustion of the sample.

COMBUSTION OF COAL

A series of tests was carried out in which, on opening the bomb after burning a 1 g sample of coal, a careful observation of the distribution of water in the bomb was made, the water on the base of the cup then being carefully pipetted off and its volume measured. It was found that the volume of water on the base was not significantly different from that of the original addition, thus confirming the fact that little of the original water is evaporated, the quantity required for saturation of the oxygen being very small. The water produced by combustion of the sample appeared to be deposited mostly on the walls and cap in the form of very fine droplets.

The important consideration when dealing with the acid-resistance properties desirable in steels used for making calorimeter bombs is the maximum concentration which may arise at any point. When calculating the concentration of the acid by which the material of the bomb is subject to attack, it has been customary to assume that the acid gases dissolve uniformly throughout the total quantity of available water, which is about 1·5 g in the case of coal (about 0·5 g being produced by the combustion of the sample). It now appeared that this might be fallacious, so a series of tests was carried out to investigate the variation of the acid concentration between the cup base and the walls and cap. The base of the bomb was coated with a silicone resin, a procedure which, it had been found in earlier tests, kept the added water in a single drop and so facilitated the removal of this water, by means of a pipette, after the combustion. The normal charging procedure was followed, but, since temperature observations were not being made, the charge was fired 2 min after assembly. The bomb was opened 5 min after firing and the residual pool pipetted from the base as completely as possible, care being taken not to collect any of the condensed droplets. The bomb cup and cap were then washed and the liquor collected in a separate flask. The two liquors were titrated against 0·05N sodium hydroxide solution using methyl red as indicator, carbon dioxide not being boiled off. The silicone coating on the base

Table 1. Distribution of acid liquor in a calorimeter bomb after combustion of 1 g of coal

Coal							*Acid in washings: ml 0·1N*			*Acid on walls and cap: % of total*
No.	*Analysis: % (air-dry basis)*						*Base*	*Walls and cap*	*Total*	
	*W**	*A*†	C	H	Cl	S				
Benzoic acid	*Nil*	*Nil*	68·85	4·95	*Nil*	*Nil*	0·57	5·98	6·55	91·3
Coal 487	13·2	2·87	68·30	4·36	0·35	0·51	0·95	10·16	11·11	91·4
Coal 23	3·3	3·40	—	—	0·30	1·00	1·44	15·12	16·56	91·3
Coal 308	2·8	2·33	80·10	4·98	0·20	1·66	2·86‡	13·45‡	16·31‡	82·4‡
Coal 303	1·5	4·41	78·38	5·20	0·31	2·01	2·43	16·12	18·55	86·9
Coal 17	0·9	4·94	—	—	—	3·28	5·70	18·94	24·64	76·9
Coal 10240	4·3	8·70	—	—	—	5·53	6·72	29·42	36·14	81·3

* *W* = moisture content. † *A* = ash. ‡ Excluding one test of doubtful accuracy.

was renewed after each test. Benzoic acid (1·2 g samples) and six coals (1 g samples) were used, each being tested in quadruplicate. The details of the fuels and the mean results of the determinations are recorded in *Table 1.*

As expected, the total acidity increased with the sulphur content of the fuel. The acidity of the liquor both on the base and elsewhere increased with the sulphur content, but despite the greater volume of the liquor of the base the amount of acid it contained was always very much less than that in the liquor elsewhere. Generally, at least four fifths of the total acid was on the walls and cap, whereas the volume of this liquor was only about one third of the total.

Taking the volume of walls–cap liquor to be 0·5 ml, the average concentrations of acid in this liquor were as given in *Table 2.* In the calculation of the

Table 2. Concentration of acids in liquor on walls and cap after combustion of 1 g of coal

Fuel	*Sulphur* %	*Total acid normality*	*Concentrations: % by weight*		H_2SO_4: *% per 0·01 g* S
			HNO_3	H_2SO_4	
Benzoic acid	*Nil*	1·20	6·8	*Nil*	—
Coal 487	0·51	2·03		4·0	7·8
Coal 23	1·00	3·02		8·3	8·3
Coal 308	1·66	2·69		6·9	4·2
Coal 303	2·01	3·23		9·2	4·5
Coal 17	3·28	3·79		11·5	3·5
Coal 10240	5·53	5·88		19·3	3·5
				Mean	5·3

individual acid concentrations, hydrochloric acid has been ignored (the effect is very small) and the nitric acid concentration has, in each case, been taken as that equivalent to the walls–cap acid in the case of benzoic acid (5·98 ml 0·1N), a procedure justified (for coal) by the work reported in Part IV of this series[1].

If the acid dissolved uniformly in the water (1·0 g of added water and 0·5 g of water from the fuel), 1 per cent of sulphur on 1 g of coal would give 2 per cent sulphuric acid in the liquor, but the observed mean concentration on the walls and cap is 5·3 per cent sulphuric acid per 0·01 g of sulphur, which is much higher than hitherto assumed.

The assumption that acid mist will settle if allowed to stand for 30 min (as advised in *B.S. 1016: 1942*[3]) has been shown by Z. K. A. MOSZYNSKI[4] to be fallacious and the present results show that this practice could, by permitting prolonged contact with the acid liquor, lead to corrosion of a steel which is not strongly corrosion-resisting. This effect may have led to a corrosion pattern often observed on the upper walls of certain bombs. It is strongly recommended that a bomb should be washed out as soon as possible after every combustion made within it. In the new *British Standard*[5] for the determination

of the calorific value of solid fuels, no period of standing before opening is advised.

COMBUSTION OF COKE

It was clear that, if similar considerations applied in the case of coke, the necessity for quick washing-out of the bomb would be still more urgent, for the concentration of acid in the walls–cap liquor would be even higher than with coal, owing to a smaller quantity of water being produced from the fuel of lower hydrogen content. A series of tests was therefore carried out to investigate the distribution of acid in a calorimeter bomb after the combustion of 1 g of coke. In accordance with the recommendations made in Part I of this series[6], the samples were burnt on a layer (0·7 g) of alumina in an Inconel crucible, of 1·5 in. diameter, with a lining of asbestos paper; the initial oxygen pressure was 25 atm (gauge). Eight cokes were used, at least two tests being performed with each according to the procedure described in the previous section. Before each test the bomb walls were carefully dried, the base coated with silicone resin and 1 ml of water pipetted on to the base. Analytical data and the mean results are given in *Table 3*.

Table 3. Distribution of acid in a calorimeter bomb after combustion of 1 g of coke

No.	*Coke*						*Acid in washings: ml 0·1N*			*Acid on walls and cap: % of total*
	Analysis: % (air-dry basis)						*Base*	*Walls and cap*	*Total*	
	W	*A*	C	H	Cl	S				
500	0·29	8·13	—	—	—	0·66	0·09	2·22	2·31	96·1
496	1·43	7·34	88·64	0·59	*Nil*	0·71	0·12	2·13	2·25	94·7
497	1·10	7·90	89·48	0·34	*Nil*	0·72	0·22	3·40	3·66	92·9
*DCU47**	3·08	5·77	81·16	2·37	0·34	1·13	0·29	6·52	6·81	95·7
357	1·71	10·22	85·18	0·47	0·28	1·16	0·06	4·44	4·50	98·7
3EII	0·16	6·35	90·52	0·23	0·02	1·80	0·60	6·54	7·14	91·7
360	2·80	12·36	79·52	1·28	0·22	2·23	0·36	7·45	7·81	95·4
54B†	0·52	10·60	82·44	0·46	0·24	5·33	3·34	25·45	28·79	88·4

* Coalite. † Pitch coke.

The mean percentage of the total acid found on the walls and cap was 94·2, compared with 85·0 for six coals in the previous series. The reason for this difference is probably that, with coal, more liquor falls from the cap to the base owing to the condensed droplets being bigger in the case of the fuel of the higher hydrogen content. Thus there is another factor making for high local acid concentrations after the combustion of coke.

The quantity of water condensed on the walls and cap may be calculated from the moisture and hydrogen contents; then, knowing the quantity of acid in this liquor, the acid concentration may be calculated. The concentration of sulphuric acid in the walls–cap liquor was calculated by subtracting, from the total quantity of acid, the quantities of nitric and hydrochloric acids. All the chlorine was assumed to be converted to hydrochloric acid, a uniform amount of 2 ml of 0·1N nitric acid was assumed to be formed and 94 per cent of these two acids assumed to be present in the walls–cap liquor. The results of

these calculations are recorded in *Table 4*; coke No. 500 is not included as, owing to the exhaustion of the sample, the required analyses could not be carried out.

Table 4. Concentration of sulphuric acid in liquor on walls and cap after combustion of 1 g of coke

Coke		*Sulphuric acid: % by weight*
No.	*Sulphur: %*	
496	0·71	1·9
497	0·72	16·5
DCU47	1·13	6·8
357	1·16	13·4
3EII	1·80	52·4
360	2·23	15·4
54B	5·33	73·3

The values for the concentration of sulphuric acid must be regarded as theoretical maxima which will be approached but not achieved for two reasons: (*a*) the evaporation and condensation on the walls and cap of a very small quantity of water from the 1 ml placed in the bomb would have a marked diluting effect, 0·02 g being sufficient to halve the concentration in the case of coke 3EII; (*b*) under the normal conditions of the routine determination of calorific value, there will be, in each test, a film of water present on the walls of the bomb as a residue from the washing out operation after the previous test and this, again, will result in a more dilute liquor being produced. Quantitative tests have shown the weight of residual water on the cup walls to be 0·45 g after 5 sec and 0·32 g after 10 min draining; such water, however, is unlikely to be evenly distributed and some will drain to the base when the cup is stood upright, so that the diluting effect is likely to be considerably less than would be indicated by a calculation based on the total quantity. Further, the two diluting effects (*a* and *b*) will be partially offset by the tendency for condensed droplets to fall from the cap or drain down the walls. It must be concluded, therefore, that the sulphur of a fuel is dissolved almost entirely in the water produced on combustion of the fuel, that acid concentrations much higher than those expected on the basis of a calculation previously used (uniform solution of the acid gases throughout the total quantity of water present in the bomb) can occur, and that the acid concentrations are higher with coke than with coal.

In an attempt to reduce the acid concentration by artificially increasing the quantity of water on the walls and cap, tests were carried out with coke 54B in which various quantities of water were added (from a microburette) to the 1 g samples after drying at 110°C. The effect on the acid concentration was as had been hoped, the addition of 0·1 ml, for example, reducing the value to less than half that shown in *Table 4*. Unfortunately, it was noticed that, if more than 0·05 ml of water was added, a small quantity of unburnt coke remained in the crucible at the point of addition of the water, so that the permissible increase in the equivalent moisture content when using this simple procedure is limited to 5 per cent. Another method of increasing the moisture

content of the coke sample (as fired) was tried: this involved standing a thin (5 mm) layer over water in an enclosed space (a desiccator used as a humidifier). In this way, the moisture content of a sample of natural graphite was increased from 0·32 per cent (air-dry) to 0·54 per cent in 24 h and to 0·88 per cent in 96 h, whilst that of a coke was increased from 0·38 per cent (air-dry) to 0·52 per cent in 24 h and to 0·60 per cent in 48 h. The increased moisture contents of these two materials did not prevent the achievement of complete combustion in a calorimeter bomb, but the added water per 1 g portion would not have been sufficient with either coke 3EII or coke 54B to halve the acid concentration of the walls–cap liquor. It is therefore recommended that, with cokes of high sulphur content and low hydrogen and moisture contents, 0·05 g of water should be added from a microburette to the 1 g sample in the crucible in order to prevent extremely high local acid concentrations arising on the walls and cap. It must be recognized, however, that the restriction of the addition from a microburette to 0·05 g is rather difficult; consequently, operators are warned to examine the crucible carefully after the determination for signs of incomplete combustion (which invalidates the result of the determination), which will probably result if more than the advised quantity of water is inadvertently added. Another feature of the data of *Table 4*, namely, the effect of the sulphuric acid concentration on the validity of the sulphur correction, is considered later.

Examination of the data of *Table 3* shows that the quantity of acid present in the bomb after the combustion was generally less than was to be expected from the sulphur and chlorine contents of the coke. It was therefore decided to investigate the distribution of sulphur in the bomb after the combustion of a 1 g sample of coke under the recommended conditions. Seven of the eight cokes of *Table 3* were used, the amounts of sulphur in the solid, liquid and gaseous phases being determined in each case. The gaseous-phase sulphur was absorbed in 10-volume hydrogen peroxide by passing the gas through a No. 2 porosity sintered-glass disc into the reagent; for this purpose, the bomb (of $\frac{1}{3}$ l. capacity) was fitted with a slow-release valve and gas release begun 5 min after firing. The solid-phase sulphur was extracted from the residue in the crucible with dilute hydrochloric acid, the solution then being filtered. The liquid-phase sulphur was present in the bomb washings, which included liquor which had been used to wash the outside of the crucible. The sulphur in each of the three solutions was estimated gravimetrically by precipitation as barium sulphate, 25 ml of a solution containing 0·6 g/l of potassium sulphate being used to seed the solutions representing the solid and gaseous phases. *Table 5* records the results as the means of at least duplicate tests. The sulphur balance is good, except for cokes DCU47 and 3EII.

The proportion of the total amount of sulphur found in the crucible is fairly constant. Further investigation showed that much of the sulphur in the crucible was present as aluminium sulphate in the alumina pad. If it were all so present (the heat of reaction of sulphuric acid with alumina being 0·096 cal/mg of sulphur), the corresponding mean error in the sulphur correction when using an independently determined value of the sulphur content (S per cent, as fired) would be an underestimate of $S \times 2{\cdot}13 \times 0{\cdot}096 = 0{\cdot}20\ S$ cal per 1 g sample.

In the gaseous phase, both the amount of sulphur and the proportion of the total sulphur vary quite widely, but the average percentage deviation from the mean is less for the former and the mean agrees well with the value (0·07 per cent of sulphur in the sample) reported in Part IV of this series[1] for six coals burnt with and without an alumina layer. As the quantity of sulphur

Table 5. Distribution of sulphur in a calorimeter bomb after combustion of 1 g of coke

Coke		*Sulphur: equivalent % of air-dry coke*				*% of total sulphur*		
No.	*Sulphur %*	*Gas*	*Washings*	*Crucible*	*Total*	*Gas*	*Washings*	*Crucible*
500	0·66	0·04	0·37	0·11	0·52	7·8	71·0	21·2
496	0·71	0·04	0·46	0·18	0·68	6·1	67·7	26·2
DCU47	1·13	0·03	0·98	0·30	1·31	2·1	75·0	22·8
357	1·16	0·06	0·81	0·19	1·06	5·6	76·7	17·7
3EII	1·80	0·05	1·04	0·27	1·36	3·6	76·5	19·9
360	2·23	0·11	1·67	0·43	2·21	5·0	75·6	19·4
54B	5·33	0·07	4·21	1·21	5·49	1·2	76·8	22·0
Mean		0·06	—	—	—	4·5	74·2	21·3
Av. % deviation		33	—	—	—	42	—	8·1

involved is very small, the mean equivalent percentage of the coke may be used. The corresponding error in the sulphur correction when using an independently determined value of the sulphur content is an overestimate, due to the heat of solution of the sulphur trioxide which remains in the gaseous phase, equal to $1{\cdot}54 \times 0{\cdot}6 = 0{\cdot}92$ cal per 1 g sample. 1·54 cal/mg of sulphur is the value quoted in Part IV of this series[1] for the heat of solution of sulphur trioxide; its implications in terms of the concentration of the sulphuric acid produced are considered later.

Thus, when using an independently determined value of the sulphur content as the basis of the sulphur correction, the error in the correction may be computed to be an overestimate of $(0{\cdot}92–0{\cdot}20\ S)$ cal per 1 g sample. Thus it may be concluded that, under these conditions, the error is negligible. This conclusion is not affected by the variability of the amount of sulphur in the gaseous phase nor by the fact that some of the sulphur in the crucible is present as sulphuric acid absorbed by the asbestos. The former consideration implies that the true value of the 'constant' term in the expression for the error actually varies somewhat; the latter implies that the coefficient of S may be a little too high.

If it is desired to compute the sulphur correction from the bomb washings, it is clear that a significant error will arise if the residue in the crucible is ignored. To see whether fixation in the crucible could be eliminated simply, or at least considerably reduced, tests were carried out in which the effects of using a fused alumina disc and of dispensing with the asbestos paper lining were investigated.

Table 6 records, as the means of duplicate tests, the amounts of sulphur present in the crucible after the combustion of five cokes (1 g samples)

under the various conditions; the results for loose alumina with an asbestos lining are taken from *Table 5*.

It is clear that the use of a fused alumina disc has little beneficial effect in reducing the degree of fixation of sulphur in the crucible. On the other hand, when the asbestos-paper lining is dispensed with, an appreciable reduction occurs, particularly when the sulphur content of the coke is very high (54B).

Table 6. Amount of sulphur present in crucible after combustion of 1 g of coke under different conditions

Coke No.	*Sulphur: % of air-dry coke, for different crucible conditions*			
	Loose Al_2O_3		*Fused* Al_2O_3 *disc*	
	With asbestos	*Without asbestos*	*With asbestos*	*Without asbestos*
496	0·18	0·12	0·17	0·07
DCU47	0·30	0·16	0·34	0·19
3EII	0·27	0·18	0·63	0·20
360	0·43	0·34	0·53	0·21
54B	1·21	0·36	1·18	0·32

However, even for cokes of normal sulphur content, the amount of sulphur left in the crucible when not using an asbestos lining is sufficient to cause an error in the sulphur correction of *ca.* 5 cal if the residue in the crucible is ignored. Moreover, if an asbestos-paper lining is not used in the crucible, the introduction of the sample in such a way as to prevent any coke particles coming into contact with the walls of the crucible (a condition necessary to ensure complete combustion) is a rather difficult operation, calling for practice and dexterity. It is concluded, therefore, that, when the sulphur correction is to be estimated from the bomb washings, the usual crucible conditions (loose alumina, asbestos lining) should be employed but that the contents of the crucible including the asbestos lining after the combustion should be taken into the bomb washings.

In this case, the error in the sulphur correction will be composed of underestimates due to the thermochemical effect of the sulphation of the alumina (maximum 0·20 S cal per 1 g sample) and the heat of formation (from sulphur dioxide) of sulphur trioxide which is not dissolved. Using the value quoted in Part IV of this series[1], the latter contribution is equal to $0{\cdot}73 \times 0{\cdot}6 = 0{\cdot}43$ cal per 1 g sample, giving a total underestimate of $(0{\cdot}20\ S + 0{\cdot}43)$ cal, which is negligible.

When determining the calorific value of a coke, it is necessary to collect and titrate the bomb washings, even when an independently determined value for the sulphur content is available for making the sulphur correction; this is because the nitrogen correction must be assessed in each determination on materials which burn slower (or faster) than coal (or benzoic acid). In this case, the crucible residue can be ignored and the washings titrated directly for the total acidity. To obtain the quantity of nitric acid in the washings, it is

necessary to subtract the quantity of sulphuric acid, and this, it is now clear, must not be calculated from the true sulphur content of the coke. To allow for the sulphur in the gaseous and solid phases, the effective sulphur content of the coke must be taken as $(S - 0{\cdot}06 - 0{\cdot}213\,S) \simeq 0{\cdot}8\,S - 0{\cdot}06$ per cent, whence the quantity of sulphuric acid in the washings can be calculated from the weight of the sample and the equivalence of 1 mg of sulphur to 0·624 ml of 0·1N sulphuric acid.

VALIDITY OF THE SULPHUR CORRECTION

The value usually quoted for the sulphur correction is 2·26 cal/mg of sulphur. The correction actually has three components: (*a*) the heat of formation of sulphur trioxide from sulphur dioxide; (*b*) the heat of formation of sulphuric acid from sulphur trioxide; (*c*) the heat of solution of sulphuric acid. Using data from the *Chemical Engineer's Handbook*[7], *a* may be computed to be 0·74 cal/mg of sulphur and *b* to be 0·97 cal/mg of sulphur; the difference between the total of these and the quoted value for the sulphur correction gives *c* as 0·55 cal/mg of sulphur. In fact, the heat of solution of sulphuric acid in water depends on the concentration of the resultant solution, as shown in *Table 7* (derived from data of the U.S. Bureau of Standards[8]).

Table 7. Heat of solution of sulphuric acid in water

H_2SO_4 % *by wt*	*Heat of solution: cal/mg of* S	H_2SO_4 % *by wt*	*Heat of solution: cal/mg of* S	H_2SO_4 % *by wt*	*Heat of solution: cal/mg of* S
0*	0·72	5	0·56	50	0·44
0·001	0·71	10	0·55	60	0·39
0·01	0·67	20	0·53	70	0·33
0·1	0·63	30	0·51	80	0·25
1	0·59	40	0·48	90	0·14

* Infinite dilution.

Thus the quoted sulphur correction is valid for the formation of sulphuric acid of *ca.* 5 to 15 per cent of sulphuric acid by weight. The sulphuric acid concentrations quoted in *Table 2* suggest that this range is, in fact, generally applicable to coals, though a coal of 5·5 per cent of sulphur gave a concentration of 19 per cent and, therefore, an overestimation of the sulphur correction by $55 \times (0{\cdot}55 - 0{\cdot}53) = 1{\cdot}1$ cal. There would, in this case, be a total overestimation of the sulphur correction by $1{\cdot}1 + 0{\cdot}9 = 2{\cdot}0$ cal, 0·9 being the heat of solution of the sulphur trioxide which remained in the gaseous phase. It is clear that, for coal, no account of the error in the sulphur correction need be taken except when dealing with a sample of very high sulphur content or when aiming at great precision.

Significant errors due to the concentration of sulphuric acid could have occurred with cokes 3EII and 54B. With a coke of 2 per cent of sulphur, it is necessary to restrict the sulphuric acid concentrations to *ca.* 30 per cent by weight in order to keep the error in the sulphur correction due to this cause to under 1 cal. With a coke of 5 per cent of sulphur, the concentration

permissible on the same basis is 20 per cent by weight. For such a coke, a higher concentration is likely to occur only when the hydrogen and moisture contents are low and it has already been advised that, in order to avoid subjecting the bomb to attack by very strong acid, the moisture content of the sample should be artificially increased (in the crucible) by the addition of up to 0·05 g of water. If this recommendation is applied, and bearing in mind that, in practice, the walls of the bomb will carry a small but (in this respect) significant amount of water, it seems that, once again, the error may be taken to be negligible except in work of great precision.

CONCLUSION

This work has shown that fears as to the gross inaccuracy of the sulphur correction are groundless, how the errors may be kept to negligible proportions in routine work, and how corrections may be applied in work of high precision. The practical recommendations as regards the determination of the calorific value of coke may be summarized as follows.

(*1*) Wash the bomb out thoroughly as soon as possible after every determination.

(*2*) Drain, but do not dry the bomb cup before the next determination.

(*3*) Fire the sample under the conditions recommended in Part I of this series[6].

(*4*) With coke of over 1·75 per cent of sulphur, add 0·05 g of water to the sample in the crucible before the determination if the hydrogen content is under 0·5 per cent (air-dry basis).

(*5*) When using an independently determined sulphur content (S per cent) to make the sulphur correction, calculate the sulphuric acid in the bomb washings from an 'effective' sulphur content ($0{\cdot}8\ S - 0{\cdot}06$ per cent) when computing the nitrogen correction from the total acidity.

(*6*) When determining the sulphur correction from the bomb washings, add the crucible residue to the washings.

It should be pointed out that, when using barium hydroxide solution in the titration for total acidity (as now recommended[5]), the 'indirect method' described in Part IV of this series[1] is unnecessary, even when determining the sulphur correction for a coke from the bomb washings. The authors of that paper considered that the direct titration would be made with sodium or potassium hydroxide solution, in which case it would not be applicable in these circumstances owing to some of the sulphur being present as aluminium sulphate in the solid phase. If, however, the solution is to be titrated with barium hydroxide solution, the objection disappears, as aluminium sulphate and barium hydroxide react stoichiometrically in solution, barium sulphate being precipitated. Before proceeding with the titration, however, the diluted washings (plus residue) must be boiled and filtered.

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An Improved Method for Determination of Coking Value of Binders used in Carbon Electrode Manufacture

L. P. CHARETTE AND L. GIROLAMI

The Norske method has been used hitherto for the determination of coking value of binders in the smelters of the Aluminum Company of Canada, Ltd, and associated companies. However, results obtained by this method are much dependent on analyst's technique. In an effort to improve the procedure, the effects of heating rate and of coking temperature on coking value have been studied. The results of this investigation led to a radically modified Norske-type procedure which is simple, fast, and considerably more precise than the original Norske method. This conclusion is supported by statistical evaluation of results from interlaboratory testing.

THE various binder pitches used in the aluminium industry for the manufacture of carbon electrodes are of coal tar or petroleum origin, and may exhibit pronounced differences on the basis of their mode of production.

One of the properties of interest to the consumer is the 'coking value' which is a measure of the pitch coke residue remaining after baking of electrode mixes. We have previously shown that a combination of the atomic carbon: hydrogen ratio and the coking value of a pitch could be correlated to pitch quality, as expressed by the compressive strength of test electrodes prepared from the pitch and a standard aggregate[1]. However, there are several methods for determining coking value and, since the experimental conditions of these methods may differ greatly, the results are not always strictly comparable. Some procedures are adaptations from tests originally developed for quite different purposes[2–5], others are specific for pitch[6–9].

In the smelters of the Aluminum Company of Canada, Limited, the 'Norske' procedure has been in use for many years. It was developed more than 20 years ago by Elektrokemisk A/S, a Norwegian aluminium producer. The procedure,[7] briefly, is as follows: place a suitable sample in a 40 ml porcelain crucible, heat carefully over a gas flame to expel volatile matter. Cover, then place in a 100 ml nickel crucible, pack with calcined coke of -20 $+65$ mesh size, and heat at 600° to 700°C for 5 hours. The coke residue obtained by this procedure is then weighed, and per cent residue calculated and reported as coking value.

In general, Norske coking values have been quite satisfactory; they could be fairly well correlated to binder economics in the aluminium smelters. However, with smelter expansion and increased production control requirements, the method was used more often and some drawbacks became apparent; the preheating step in the method was subject to a high personal factor, and agreement between analysts and between laboratories was found to be poor.

In an effort to work out a technique with improved precision, an investigation was therefore undertaken to study coking conditions in the Norske procedure. Because of production and specification reasons, any new or improved coking value method had to give results substantially equal to those of the existing Norske method.

STUDY OF COKING CONDITIONS

Preliminary investigations

The quantity of coke formed during a coking value test was assumed to depend, among other factors, upon the heating rate to which the binder is subjected before it reaches the final coking temperature. Lack of control in the preheating step of the Norske method was believed to be the cause of poor reproducibility.

After exploratory tests had indicated that coking value changed significantly with heating rate, a series of experiments was carried out to study this effect

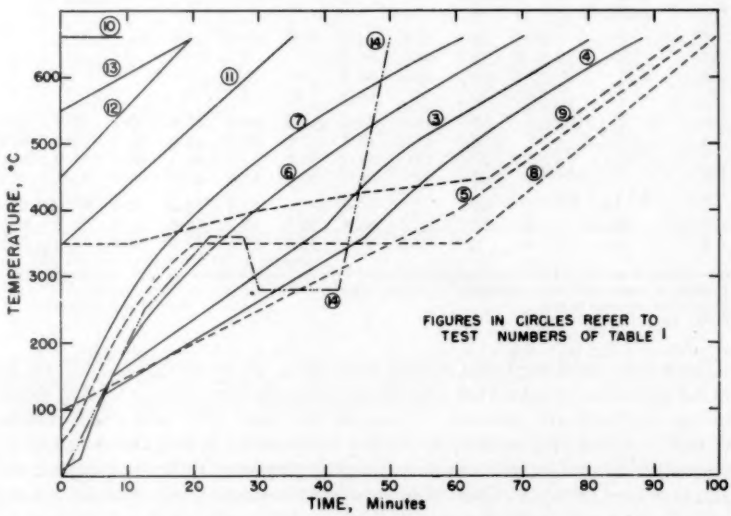

Figure 1. Preheating patterns. Tests on determination of coking value with controlled rate of heating

in greater detail. In these tests, general conditions were those used for the standard Norske method: the porcelain crucible containing the pitch sample was covered and packed in calcined petroleum coke in a nickel crucible. The crucible was then charged into a Lindberg laboratory furnace and preheated according to the heating curves shown in *Figure 1*. Coking values obtained after final heating at 660°C for varying periods are compared in *Table 1* to those obtained by the Norske method. At medium preheating rates, such as those indicated by curves Nos. 3, 4, 6 and 7, the rate apparently did not have much effect on the amount of pitch coke produced. However, at a slow rate

(curve 5) or by keeping the sample at a certain temperature level for some time (curve 8), a larger amount of coke was produced. This was also the case when samples were placed into the preheated furnace at 350°C (curve 9) and subsequently heated slowly to 660°C. With rapid preheating rate or high initial temperatures (curves 10 to 13), the coking value decreased. In the Norske procedure, that is with preheating over a gas flame, the pattern was roughly that indicated by curve No. 14.

Table 1. Effect of heating conditions on per cent coking value of pitch
(Data listed in order of decreasing heating rate. Sample size, 3 g)

Test No.	*Final heating at 660°C*. Time in hours*	*Pitch Identification No.*									
		46	72	73	87	89	90	94	103	106	107
14	5 (*Norske method*)	53·3	62·2	59·4	64·8	57·9	53·8	47·9	49·6	54·4	49·5
10	2	49·7	54·9	52·8	60·7	53·3	50·8	43·4	46·2	52·5	†
13	1	54·0	57·3	53·3	63·8	†	†	†	†	†	†
12	1	52·2	58·1	55·8	64·2	†	†	†	†	†	†
11	1	52·6	58·7	‡	64·4	†	†	†	†	†	†
7	1-1/12	†	60·1	58·2	65·6	57·4	54·4	47·6	50·1	55·7	50·4
6	1-1/4	†	60·3	58·8	65·8	57·6	54·5	48·0	49·9	56·6	50·8
3	1	†	60·2	58·4	66·4	58·0	55·1	48·5	49·6	55·9	50·9
4	1	†	60·3	‡	66·1	57·4	54·9	47·9	50·0	56·5	50·8
5	5/6	†	61·1	‡	67·0	‡	55·5	48·6	50·4	57·4	51·5
9	1	†	62·2	61·1	67·8	58·8	56·2	50·6	51·1	56·2	52·4
8	1	†	‡	60·0	71·0	58·9	57·1	48·9	51·9	58·4	54·5

* Preheating was carried out according to curves in *Figure 1.*
† Sample not included in test.
‡ Boiled over.

These tests confirmed that coking value may, under certain conditions, be varied with heating rate. They also showed that the temperature level at which coking reactions are allowed to proceed for some time will affect results. Actually, coking at a steadily increasing temperature may be regarded as an integration of coking at successively higher temperature levels at which the sample is kept for a very short time. It would thus appear possible that coking carried out at a suitable temperature level would give the same coking value as that obtained by coking the sample slowly through a temperature range. Such a procedure obviating control of heating rate would appear advantageous in several respects; for example, cooling down and reheating of equipment would be avoided, and in general simpler equipment would be required.

Influence of coking temperature on coking value

A series of experiments was then made to determine the amount of coke produced by direct heating at various temperature levels. The results obtained are shown in *Table 2.*

Coking at the relatively low temperature of 450°C proceeded rather slowly. After 1 and 2 hours coking, the pitch cokes still had a strong 'tar' smell.

Although this was no longer perceptible after 15 hours heating, coking could not be regarded as complete in view of the substantial loss in weight taking place upon additional heating at 660°C. Weight losses after further heating at 950°C were of the same order of magnitude. Coking values by direct heating at 450°C were higher than by the regular Norske method.

Table 2. Per cent coke yields obtained in tests with direct heating
(Sample size, 3 g,)

Temperature °C	*Duration of heating*	*Pitch Identification No.* 4	46	68	72	73	87
450	1 h	*	62·3	65·7	64·9	66·1	82·5
	2 h	*	60·0	62·8	64·1	65·8	80·9
	15 h	31·0*	58·0	61·1	62·2	62·2	71·1
	†	30·0	56·8	59·8	60·7	61·4	69·6
	‡	28·8	55·2	59·3	59·3	60·1	67·8
660	15 min	41·1	49·9	53·0	56·5	52·6	62·5
	1 h	41·3	49·7	52·4	55·3	53·8	61·3
	2 h	41·9	49·7	—	54·9	52·8	60·7
950	15 min	36·6	45·2	47·7	53·4	46·1	56·7
	30 min	36·9	—	47·6	52·4	48·6	56·4
550	1 h‖	44·5 (44·0)§	54·6 (54·0)	57·6 (57·2)	59·9 (59·4)	57·7 (57·1)	66·1 (65·5)
	2 h‖	45·0 (44·5)	54·6 (54·1)	56·9 (56·0)	59·6 (59·4)	57·4 (57·1)	65·8 (65·1)
Norske method	—	45·0	53·3	58·4	62·2	59·4	64·8

*Sample boiled over.
†Additional heating at 660°C for 30 minutes.
‡Additional heating at 950°C for 15 minutes.
§ Results in parentheses were obtained after 20 minutes of additional heating at 660°C.
‖One gramme sample used.

A similar test was run at 660°C. At this temperature, the coking value was definitely lower than with the Norske procedure. It was still more so in another series of determinations carried out at 950°C.

Since results at 450° and 660°C were respectively higher and lower than those found by the Norske method, an intermediate temperature of 550°C was tried next. The results obtained are also shown in *Table 2.*

These preliminary results at 550°C seemed to agree reasonably well with the accepted Norske values. It should be mentioned that the sample size had to be reduced to 1 g because boiling over occurred occasionally 3 g samples; this change did not affect the results. Differences between values after 1 and 2 hours heating were negligible. Thus coking at 550°C seemed reasonably complete, and additional heating at 660°C only slightly reduced the weight of the coke residue. The completeness of coking was further evidenced by a few coking tests using a Chevenard thermo balance, which indicated that loss of weight set in at about 140°C and was over, for practical purposes, at a temperature slightly below 550°C. In this respect it should be realized that completeness of coking as estimated by weight losses might not coincide with the true completeness of coking; in other words,

although heavy volatiles are driven off completely below 550°C, further coking involving evolution of light gases such as hydrogen might still proceed. The small weight changes involved, however, are of no significance in a practical coking value test.

An important factor in the procedure appeared to be the size of the

Table 3. Comparison of coking values obtained by Norske method, direct heating at 550°C and method using controlled preheating

Pitch No.	*% Coking value**					
	Norske method (Analyst B)	*Direct heating, 550°C*				*Method using controlled preheating*
		Lindberg furnace		*Hoskins furnace*	*Average*	
		(Analyst A)	*(Analyst B)*	*(Analyst B)*		
4	45·0	44·9	45·2	47·9	46·0	46·5
15	65·7	68·3	67·7	68·5	68·2	65·1
22	65·1	65·3	65·0	66·4	65·6	65·9
23	42·9	40·6	41·1	43·0	41·5	44·7
24	38·9	33·3	33·9	34·5	33·9	33·5
46	53·3	54·6	54·8	55·8	55·1	50·4
53	51·7	50·7	50·7	50·9	50·7	48·8
55	51·1	—	51·9	53·3	52·6	49·6
60	59·9	61·4	61·5	62·3	61·7	61·7
62	55·3	56·1	57·1	58·0	57·1	54·8
63	58·6	58·3	57·1	57·4	57·6	55·0
68	59·4	57·7	56·9	58·2	57·6	54·1
72	62·2	59·7	59·6	60·8	60·0	57·6
73	59·4	57·6	58·2	59·3	58·4	56·4
74	51·7	49·2	50·4	51·1	50·2	47·5
75	53·5	50·1	51·1	51·0	50·7	49·1
77	53·7	52·7	53·0	53·8	53·2	51·4
78	57·9	58·0	58·7	59·8	58·8	58·6
82	56·9	57·2	58·6	57·6	57·8	54·4
83	58·5	54·9	56·0	55·9	55·6	52·6
87	64·8	65·3	65·9	65·8	65·7	63·0
88	55·6	53·0	53·9	54·6	53·8	52·1
89	57·9	57·1	57·4	57·3	57·3	53·6
90	54·3	54·2	54·4	56·0	54·5	52·1
91	54·1	50·2	49·9	50·7	50·3	47·9
92	50·0	47·8	48·6	49·6	48·7	47·5
93	51·0	49·8	49·7	50·3	50·0	47·8
94	47·9	47·3	47·7	48·6	47·9	45·4
96	51·0	48·5	—	49·2	48·9	44·7
98	49·1	47·7	47·9	48·9	48·2	46·2
103	49·5	49·2	49·9	50·2	49·8	48·1
106	54·6	55·2	55·7	57·3	56·1	54·4
116	58·5	56·8	57·5	58·9	57·7	55·8
117	52·9	52·5	52·8	53·6	52·9	51·0
121	57·2	57·6	58·3	58·4	58·1	55·6
122	54·8	52·2	52·8	54·0	53·0	51·1
Overall averages	54·6	53·7	54·1	54·9	54·0	52·0
Standard deviation†	1·5	0·65	0·57	0·35	0·53	—

* All values are averages of at least two determinations.
† Standard deviations were calculated from replicate determinations on individual samples.

calcined coke used to provide a protecting blanket of a mixture of carbon monoxide and carbon dioxide. With the specified coke size (−20 +65 mesh) adequate protection is provided. A coarser size fraction used in one instance led to a series of low coking values because of some actual combustion of the sample.

COKING VALUE BY DIRECT HEATING AT 550°C

The 550°C direct heating procedure, which is described below in detail, was more thoroughly tested by determining coking values of a large number of pitch samples. The results obtained are compared in *Table 3* with the values found by the Norske procedure.

Apparatus required

Muffle furnace, equipped with indicating pyrometer controller and maintained at 550°C. During the determination, this temperature should not go below 540°C and not above 560°C. The heating characteristics of the furnace should be such that, after the inevitable drop in temperature upon inserting the samples, the proper temperature (550°C) should be reached within 10 to 15 minutes. The use of a Hoskins muffle furnace (Fisher Scientific Company, Ltd, Cat. No. 10–526, FH–204) provided with a suitable pyrometer controller (e.g. Foxboro pyrometer controller), is recommended. A Lindberg box-type furnace, model B–6, with indicating pyrometer controller (Fisher Cat. No. 10–539) has also been found suitable.

Sample preparation

When sufficiently hard, the analytical sample should be ground to pass at least a 20 mesh sieve (preferably 65 mesh) using a small jaw crusher followed by a mortar and pestle, or a rolling pin made of tool steel. In warm weather a preliminary chilling of the sample in a refrigerator is of assistance to this. In the case of pitches too soft for grinding, the sample may be melted, mixed, and small amounts poured out for analysis, or may be broken up with a hammer and the pieces used; it is also possible to transfer suitable portions of soft pitch using a spatula or other suitable tool, without preliminary melting. The melting temperature must not exceed 150°C, and the melting period should not be longer than 10 minutes.

Procedure

(*a*) Ignite and weigh a high form No. 1 porcelain crucible (30 ml capacity) provided with a cover. Weigh 1 g of the sample into the crucible, cover with the porcelain lid, and place in a 100 ml nickel crucible by means of a wire hook (see *Figure 2*). Pour screened calcined coke

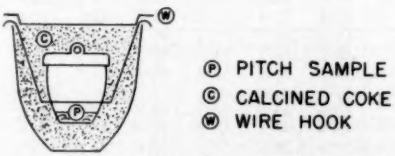

Figure 2. Position of sample with porcelain crucible in nickel crucible

(−20 to +65 mesh) into the nickel crucible so that the porcelain crucible is completely *embedded* in the coke, taking care to avoid contamination of the sample with coke particles. Cover with a nickel lid.

(*b*) Insert the crucibles *as quickly as possible* (to avoid large heat losses) into the muffle furnace. For effecting this transfer a suitable crucible tray should be used. The crucibles should be placed so that there is not less than ¼ in. of space between bottom (and sides)

of the nickel crucible and floor (and walls) of the muffle. There should be not less than 2 in. of space between the crucibles and back, and between crucibles and door of the furnace.

(*c*) After 2·5 hours, remove the crucibles from the furnace and allow to cool. Lift the porcelain crucible out of the coke by means of the wire hook, brush and wipe free from adhering dust, taking care to avoid contamination by coke particles. If necessary, place in a desiccator to cool to room temperature, and weigh If greater accuracy is desired, repeat the determination and report the average value.

$$\% \text{ Coking value} = \frac{\text{Weight of residue, g} \times 100}{\text{Weight of sample, g}}$$

(*d*) To clean the porcelain crucibles and covers, discard the residue and burn off remaining carbonaceous matter by igniting at 700° to 1000°C.

Also given in *Table 3* are coking values obtained by another modification: the sample was preheated as in the Norske procedure, but the preheating was carried out under controlled conditions on a special electric hot plate; final heating was done according to A.S.T.M. method D–168–30 at 950°C. With preheating rate suitably adjusted, coking values were obtained which, at first, seemed to agree well with the Norske coking values. However, the data presented in *Table 3* show that, for the samples used in the test, the difference between results with this method and the Norske procedure was much larger than between the latter method and the 550°C direct heating procedure. It

Table 4. Intercompany evaluation of 550°C direct heating procedure for coking value

Pitch No.	*Individual laboratory averages**							*Group averages*		*Norske* ‡
	Aluminium Laboratories Limited	*Lab A*	*Lab B*	*Lab C*	*Lab D*	*Lab E*	*Lab F*	*(1) to (6)*	*(1) to (7)*	
	(1)	*(2)*	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*	*(8)*†	*(9)*	
55	52·5	50·8	50·9	51·7	51·6	51·8	49·9	51·6	51·3	52·5
60	61·7	61·3	61·3	61·8	61·3	61·2	59·9	61·4	61·2	60·7
72	60·0	60·1	59·7	60·8	60·3	60·7	59·4	60·3	60·1	61·5
73	58·3	59·0	58·3	60·6	59·1	59·2	59·3	59·1	59·1	58·4
74	50·3	50·5	49·3	51·3	50·9	51·0	48·8	50·6	50·3	51·2
77	53·2	52·7	52·9	53·5	53·4	53·4	50·8	53·2	52·9	54·7
78	58·8	59·3	59·8	60·2	59·8	60·4	58·4	59·7	59·5	59·3
83	55·6	55·3	55·4	55·8	55·7	55·6	52·6	55·6	55·1	56·0
87	65·6	65·3	64·7	65·2	66·2	65·4	63·0	65·4	65·1	64·3
88	53·9	54·1	53·3	54·5	54·3	53·9	51·2	54·0	53·6	55·3
90	54·5	54·7	*Sple lost*	54·8	54·7	53·5	52·5	54·4	54·1	54·6
92	48·6	49·6	49·8	50·3	49·9	50·4	47·9	49·8	49·5	51·0
94	47·8	48·4	48·2	49·3	48·4	48·8	47·6	48·5	48·4	49·3
116	58·0	57·9	58·7	58·4	59·1	58·5	56·2	58·4	58·1	57·9
117	53·2	53·3	53·3	54·2	53·8	52·7	50·6	53·4	53·0	53·5
Bias from assigned values (8)	−0·23	−0·21	−0·39	+0·47	+0·21	+0·07	−1·82			+0·32

* All supplier laboratories reported four values for each sample except Lab E where the last eight samples were run three times only.
In our own laboratory (column 1) 5 to 8 replicate determinations were carried out.
† These are considered the best estimates, so far obtained, of the 'true' coking values. For statistical calculations, they are referred to as 'assigned' values.
‡ Average of replicate analyses carried out in our laboratory and in two laboratories of the Aluminum Company of Canada, Ltd.

might have been possible to obtain results in closer agreement by this modified method by further adjustment of the preheating rate. However, this was not attempted in view of the satisfactory agreement obtained with the undoubtedly simpler and faster direct heating procedure.

Evaluation of direct heating method

A preliminary test carried out between three of our laboratories had clearly indicated that the precision of the 550°C direct heating method was significantly better than that of the Norske procedure, and confirmed the agreement previously observed with the Norske results. A more extensive cooperative evaluation of the proposed method was then undertaken in which six pitch suppliers in the United Kingdom, United States and Canada were requested to take part.

Replicates of fifteen different pitch samples were submitted to the participating laboratories, each one being requested to carry out, by the direct heating method, quadruplicate determinations on each sample.

Averages of these replicate determinations are given in *Table 4*; for comparison purposes, Norske coking values obtained in our laboratories are also

Table 5. Repeatability and accuracy of coking value determination
(Direct heating at 550°C)

Participating laboratories	*Repeatability*		*Accuracy*	
	Degree of freedom	*Standard deviation*	*Degree of freedom*	*Standard deviation*
Aluminium laboratories Limited	83	0·76	98	0·88
A	45	0·34	60	0·47
B	42	0·88	56	0·91
C	45	0·38	60	0·69
D	45	0·68	60	0·65
E	37	0·54	52	0·61
F	45	0·91	60	2·13
Weighted average standard deviation:				
Excluding laboratory F results	297*	0·65	386*	0·74
Including laboratory F results	342*	0·69		

* These represent the total number of degrees of freedom associated with given weighted average standard deviations.

included. Due to misinterpretation of some parts of the method, laboratory 'F' obtained results which were much lower than those reported by the other laboratories; consequently, for the final statistical evaluation* of the direct heating method, these results were not taken into account.

In spite of the fact that the manner in which the test was carried out may have differed appreciably from laboratory to laboratory, which would tend to

* *Nomenclature used in statistical evaluation*
(*a*) Repeatability: A measure of deviation of single coking values from their individual laboratory sample mean value, all determinations being carried out in one laboratory (standard deviation within individual laboratory).
(*b*) Reproducibility: A measure of deviation of single coking values from their sample mean values obtained by averaging all individual sample values obtained in all laboratories.
(*c*) Assigned value: Sample average of all results obtained by all laboratories for a given sample.
(*d*) Accuracy: A measure of deviation of single coking values from assigned values.

increase the experimental error within certain laboratories, the overall or weighted average repeatability of 0·65 per cent coking value (see *Tables 5* and *7*) is considered very satisfactory. Still more significant than repeatability in procedure evaluation is reproducibility, which provides a more realistic measure of precision since it takes into account the deviations 'within' as

Table 6. Reproducibility and intercompany agreement of coking value determination
(Direct heating at 550°C)

Pitch No.	*Reproducibility**		*Intercompany agreement**	
	Degree of freedom	*Standard deviation*	*Degree of freedom*	*Standard deviation*
55	24	0·89	5	0·63
60	26	0·50	5	0·25
72	26	0·67	5	0·42
73	26	1·00	5	0·84
74	25	0·52	5	0·61
77	25	0·65	5	0·32
78	25	0·83	5	0·59
83	24	0·56	5	0·58
87	25	0·67	5	0·49
88	24	0·69	5	0·42
90	20	0·59	4	0·54
92	24	0·92	5	0·65
94	25	0·74	5	0·52
116	26	0·73	5	0·46
117	26	0·76	5	0·52
Weighted average standard deviation	371†	0·73	74†	0·52

* Excluding results from laboratory F.
† These represent the total number of degrees of freedom associated with given weighted average standard deviations.

Table 7. Minimum, maximum and average precision and accuracy data
(Direct heating at 550°C)

	Repeatability	*Reproducibility*	*Accuracy*	*Intercompany agreement*
Lowest company data	0·34		0·47	
Highest company data	0·88		0·91	
Weighted average	0·65	0·73	0·74	0·52

NOTE: The statistical data presented in this table do not include results from laboratory F.

well as 'between' laboratories. Inasmuch as the determination of coking value is not an analytical procedure in the true sense of the word and its precision depends on adherence to prescribed experimental conditions, a reproducibility of 0·73 per cent coking value (see *Tables 6* and *7*) is more than adequate. This represents about 1·3 per cent of the amount present, which even for many true analytical procedures is considered satisfactory. From a practical viewpoint, it means that one can expect that, out of 100 coking value determinations, 68 will not deviate from the mean value by more than 0·73 per cent and 95 by not more than 1·46 per cent. The intercompany agreement of 0·52 per cent as given in *Table 7* also reflects the high reproducibility of the direct heating method.

Since the 'true' coking values under conditions of the direct heating procedure were not known and since the number of determinations carried out on each sample was fairly large (at least 25), it was felt that good estimates of the 'true' coking values would be provided by the averages of coking values obtained for individual samples by all participating laboratories. These estimated or assigned values are given in column 8 of *Table 4* and were used to determine accuracy values of *Tables 5* and *7*. Individual laboratory accuracies were obtained by taking the square roots of the mean squares of the deviations of all sample determinations from the assigned values. This method of calculating accuracy offers a much better and more critical evaluation than bias or arithmetic mean deviation, since it combines both the repeatability and bias of individual samples. For instance, laboratory 'E' has a bias of only 0·07 per cent as compared to 0·21 per cent for laboratory 'A' (see *Table 4*) and yet the agreement with the assigned coking values is better for the latter (0·47 per cent against 0·61 per cent) because of its higher repeatability (see *Table 5*). Although individual laboratory accuracies show differences, they are all considered highly satisfactory.

As already emphasized, the coking value method is one where results depend entirely on test conditions. Therefore, it is reasonable to expect that, even with the fairly well-defined conditions of the proposed procedure, variations in results will be found because of unavoidable differences in equipment used and its performance. However, it is felt preferable to accept a certain degree of variation in results with a relatively simple method, rather than resort to more complicated and expensive equipment which would be required to eliminate such differences; the gain in precision might not be commensurate with the effort involved.

The apparent advantages of the proposed 550°C direct heating method over the Norske method and other procedures considered are mainly simplicity, speed and precision. It is of prime importance always to follow the same heating pattern, and temperature control is therefore quite critical; in our experience pyrometers cannot be completely trusted and regular checks with a good potentiometer are recommended.

SUMMARY

The 550°C direct heating procedure was found adequate for the determination of coking value of pitch binder for electrode manufacture. Statistical analysis of experimental data showed some variations in precision and accuracy between the various laboratories that participated in the evaluation of the method, but these differences should not be regarded as significant although they may appear real from a statistical standpoint. The various participating laboratories have agreed that this procedure is far superior to the Norske method from the standpoint of both precision and operation. The method has been adopted as standard in smelters of our producing associates and is also used by our regular pitch suppliers.

The authors wish to acknowledge the contribution of G. T. Bischofberger who conducted part of the preliminary experiments and of L. Tremblay for carrying out a considerable number of tests in the course of the development

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The Moisture in Yallourn Brown Coal and Its Relation to the Calorific Value Determination

NANCY T. ROSSITER

In an attempt to determine the total amount of water present as such in Yallourn brown coal, its drying in nitrogen and in air has been studied and the loss of weight compared with the weight of water and carbon dioxide evolved. Although the definition of the total water content presents difficulties, it has been found that these methods give an underestimation for drying periods of normal duration for both raw and 'air-dried' coal. Determinations of calorific value, with suitable corrections, enable errors to be compensated in a 'two-stage' drying procedure.

IT IS generally accepted that the drying of coal to constant weight in air at 105° to 110°C is not satisfactory as a standard procedure for determining its moisture content. Oxidation of the coal occurs during drying and the result is also affected by humidity variations in the surrounding atmosphere. However, in laboratories where many moisture determinations are carried out daily it is a practical low-cost method of obtaining comparable results.

With high moisture brown coals a common practice is to use a 'two-stage' drying procedure for the sample on which the determination of calorific value and ultimate analysis are made. It involves exposing a sample of 'as-received' coarse coal (< 0·25 in.) in air for 24 hours, crushing to pass a 72 mesh B.S. sieve and exposing to the atmosphere overnight. This introduces a possibility of error as the sample is exposed to atmospheric oxidation and if this occurs the calorific value will be lower. The question arises as to whether the errors of moisture determination and those due to oxidation of the coal during air and oven drying, are additive or compensatory in the determination of the calorific value used for the calculation of plant efficiency. This is discussed in the present paper.

EXPERIMENTAL

Sampling

All samples of coal were taken from the laboratory sample* used for daily routine moisture and ash determinations (< 0·25 in. particle size). This sample is quartered from a gross sample, taken from the bunkers of the Power Station in regular increments over the preceding 24 hours. The sample for testing was crushed to pass a $\frac{1}{8}$ in. aperture sieve (except where otherwise stated) mixed as quickly as possible and stored tightly packed in bottles with firmly fitting lids. Under these conditions of storage there was no significant drop in moisture or calorific value for the duration of the tests (maximum period 4 days). If needed, a sample was put out for air-drying as

* Samples taken from different laboratory samples are referred to throughout as different coals.

described. (A sample so treated is referred to throughout this paper as 'air-dried' coal.) Each bottle was opened once only immediately prior to testing.

Average analysis of Yallourn brown coal over the period of testing was as follows:

	Per cent	Range per cent
Moisture 'as received'	66·2	64·0 to 68·0
Ash (dry basis)	2·2	1·5 to 3·5
On a moisture and ash-free basis		
Carbon	68·2	67·6 to 68·6
Hydrogen	4·75	4·65 to 4·9
Sulphur	0·27	0·24 to 0·33
Nitrogen and oxygen (by difference)	26·78	—
Gross calorific value	11 410 B.t.u./lb	11 300 to 11 550 B.t.u./lb

Order of testing

Random order was used when the number of factors being tested was greater than the number of replications but cyclic order was preferred when the number of replications could be made equal to or an integral multiple of the factors under test.

Apparatus

'Quick-fit' weighing bottles of the squat, internal-stopper type were used. In the oven these were fitted with two-holed rubber stoppers through which the copper tubing carrying the gas stream passed. The rubber stoppers were dehydrated prior to use by heating for about 30 hours at 140°C or until the apparatus gave a low constant blank for the Anhydrone receiving tube. The Carbosorb bulb had a zero blank but both tubes were affected somewhat by variations in atmospheric conditions.

The nitrogen and air were dried and freed from carbon dioxide by passing through Anhydrone and Carbosorb; the nitrogen was also freed from oxygen by passing through copper turnings heated to 620°C. The flow rate for both operations was about 150 cm^3/min.

A Griffin–Sutton bomb calorimeter and Beckmann thermometer were used for the calorific value determinations and the corrected temperature rise was calculated on the basis of the A.S.T.M. formula[1]. The weight of coal taken was sufficient to give a rise of approximately 4°C and the bucket and jacket adjusted to 20° and 24°C, respectively.

When comparisons with air-oven moistures were made a convection ventilated oven was used.

Indeterminate end point in nitrogen-oven drying

Of the stand methods recommended for moisture determination thermal drying in nitrogen was chosen as it enabled the water evolved to be collected and weighed and this provided a direct determination of the moisture.

No reference had been found in the available literature to the indeterminate end point of this method and it was thought possible that the continued loss

of weight in nitrogen with increasing time and temperature was a peculiarity of Yallourn brown coal*.

Preliminary tests having shown that the coal drying in nitrogen at 110°C did not come to constant weight in the same time as an equal weight of coal drying in atmospheric air at the same temperature, experiments were made in an attempt to find an end point for the method. 5 g of wet and 2 g of

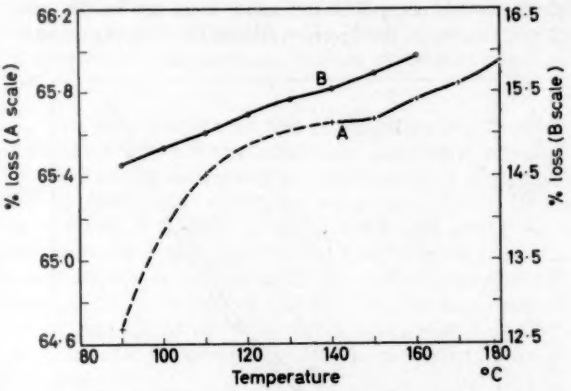

Figure 1. Weight loss/temperature curves for coals dried in nitrogen. Time constant—3 hours

\+ A. *Wet coal* (−$\frac{1}{8}$ *in.*). *Means of duplicate determinations on 6 coals.*
○ B. '*Air-dried*' *coal* (−*72 mesh B.S.*). *Means of duplicate determinations on 5 coals.*

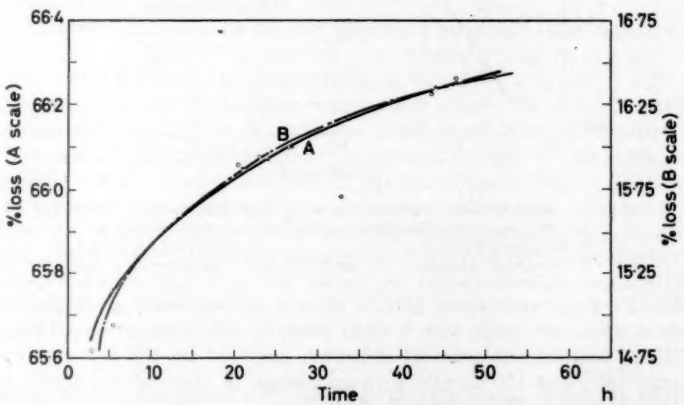

Figure 2. Weight loss/time curves for coals dried in nitrogen. Temperature constant—180°C

\+ A. *Wet coal* (−$\frac{1}{8}$ *in.*). *Means of duplicate determinations on 2 coals.*
○ B. '*Air-dried*' *coal* (−*72 mesh B.S.*). *Means of duplicate determinations on 1 coal.*

* Since writing this paper the October 1957 issue of *Fuel, Lond.* is to hand. In notes on the determination of moisture in lignite (p 469), W. W. Fowkes, J. J. Hoeppner and R. McMurtrie report this indeterminate end point in thermal drying of North Dakota lignite in nitrogen and in other inert gas atmospheres.

'air-dried' coal were used throughout all tests except for calorific value determinations. These weights were equivalent to about 1·7 g of dry coal.

Variations in loss of weight with time and with temperature were obtained for wet and 'air-dried' coal and are shown in *Figures 1* and *2*. In curve A, *Figure 1*, the points 90° and 110°C were extrapolated from differences in loss of weight at 90°, 110° and 140°C obtained with a different set of coals (8) from those for which the points 140° to 180°C were plotted. To enable the rates of drying to be compared the scales used are in the ratio wet : 'air dried' = 2 : 5; that is, in the inverse ratio of the weights taken.

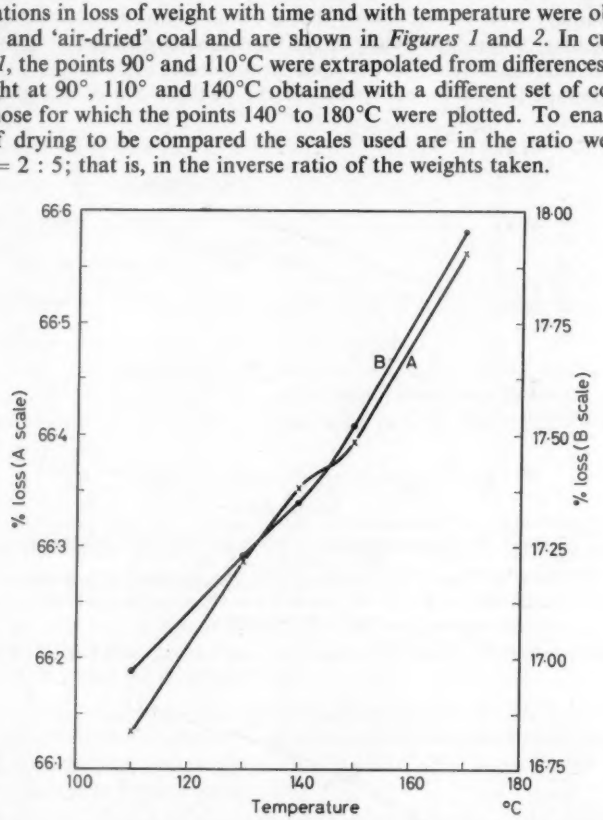

Figure 3. Weight loss/temperature curves of 'wet' and 'air-dried' samples of the same coals dried in nitrogen. Time constant—3 hours
× A. *Wet samples* (−⅛ *in.*). } *Means of duplicate determinations on 5 coals.*
⊙ B. *'Air-dried' samples* (−72 *mesh B.S.*). }

The 'air-dried' coal curve (*Figure 1*) was almost linear throughout the whole temperature range with a slight point of inflection between 130° and 150°C. A well defined point of inflection occurred on the wet coal curve between 140° and 150°C with a sharp change of slope above 150°C to a gradient parallel to the 'air-dried' curve.

In *Figure 2* the rates of loss were much the same in the wet and 'air-dried' coals; no significance could be attached to the small differences with so few samples. Both coals appeared to be close to constant weight at 47 hours.

Figure 3 shows the weight loss/temperature curves for wet and 'air-dried' samples of the *same* coals (curves A and B in *Figure 1* were different coals).

Again there was a point of inflection on the wet coal curve between 140° and 150°C and a change of slope at 140°C in the 'air-dried' coal curve, the gradients being parallel above 150°C as in *Figure 1*. It suggested that the wet and 'air-dried' coals contained a different amount of residual moisture until a temperature of 140°C was reached, that above 150°C there was a change in the drying process (or possibly decomposition) which accelerated the rate of loss and that this change occurred at a slightly lower temperature in the 'air-dried' samples. For these reasons 140°C was chosen as the highest temperature for study and because scouting tests indicated that coal dried in nitrogen above this temperature showed a deterioration in calorific value.

In order to establish whether the loss of weight on prolonged drying was due to coal being carried by the gas stream, an experiment was carried out in duplicate on two samples of wet and of 'air-dried' coal. Although details of the four tests involved varied somewhat, the general pattern was as follows. After an initial drying period of 3 hours at 140°C, the drying was continued at this temperature for a prolonged period 8 to 15 hours; this resulted in a loss of weight of approximately 0·8 mg/h. The temperature was then dropped to 110°C for 8 to 15 hours during which no further loss occurred. Finally the temperature was raised to 180°C for 3 hours with a resultant loss of 3 mg/h. This eliminated the possibility that the continued loss of weight was due to loss of coal.

The total increase in loss from 3 hours at 110°C to 47 hours at 180°C was approximately 1·2 per cent for wet and 3·0 per cent for 'air-dried' samples.

Measurement of products evolved

To obtain information as-to whether the loss of weight was due only to water evolved, the products of drying wet and 'air-dried' coal in nitrogen were collected and weighed for temperatures of 90°, 110° and 140°C with two drying periods each. At the same time as each sample was dried in nitrogen a second sample of the same coal was dried in air freed from water and carbon dioxide, the moisture dishes being side by side in the same oven. The water was absorbed in Anhydrone and the carbon dioxide in Carbosorb. With wet coals where about 3 g of water was evolved, this collected at the bottom of the U-tube and only the second arm was packed with Anhydrone. *Tables 1* and *2* give the means of determinations on four different coals for each temperature and time, the water and carbon dioxide evolved being obtained from the gain in weight of the Anhydrone and Carbosorb respectively.

There was no significant difference between the loss of weight in nitrogen and the weight of the water evolved at any time or temperature. However, as the mean loss on the 'air-dried' samples dried in nitrogen at 140°C for 2 hours was 0·15 per cent greater than the water evolved, the test was repeated with a further 9 'air-dried' coals so that a real difference if such existed would be revealed. *Table 2* shows the data for all the 13 'air-dried' coals tested and of 10 wet coals dried at 140°C for 3 hours.

Table 1. Means of percentage loss and weight of water and carbon dioxide evolved in thermal drying of coal in nitrogen and dried air (four coals)

Wet coal ($-\frac{1}{8}$ *in.*)

Temp. °C	Time h	Nitrogen				Air			
		% Loss (L)	% Gain (G)		G − L	% Loss (L)	% Gain (G)		G − L
			H_2O	CO_2			H_2O	CO_2	
90	3	65·06	65·03	0·07	0·04	65·07	65·36	0·18	0·47
	5	65·73	65·71	0·07	0·05	65·47	65·84	0·25	0·62
110	2	65·14	65·08	0·06	0·00	65·36	65·58	0·20	0·42
	3	65·79	65·75	0·10	0·06	65·66	66·11	0·30	0·75
140	2	65·80	65·84	0·12	0·16	65·74	66·38	0·44	1·08
	3	65·89	65·91	0·14	0·16	65·81	66·63	0·60	1·42

'Air-dried' coal (*−72 mesh B.S.*)

Temp. °C	Time h	Nitrogen				Air			
		% Loss (L)	% Gain (G)		G − L	% Loss (L)	% Gain (G)		G − L
			H_2O	CO_2			H_2O	CO_2	
90	3	14·13	14·21	0·19	0·27	13·93	14·49	0·37	0·93
	5	14·41	14·43	0·21	0·23	14·15	14·83	0·41	1·09
110	2	14·47	14·50	0·22	0·25	14·21	14·96	0·49	1·24
	3	14·52	14·58	0·22	0·28	14·30	15·19	0·57	1·46
140	1	14·72	14·67	0·26	0·21	14·57	15·57	0·84	1·84
	2	14·86	14·71	0·40	0·25	14·63	16·11	1·26	2·74

Table 2

Wet coals		*'Air-dried' coals*	
140°C—3 hours—nitrogen		*140°C—2 hours—nitrogen*	
Loss of weight %	*Wt of water evolved %*	*Loss of weight %*	*Wt of water evolved %*
66·58	66·56	15·56	15·30
67·18	67·20	16·57	16·59
64·19	64·20	15·29	15·06
67·33	67·34	14·35	14·28
66·36	66·42	14·24	14·19
65·50	65·50	14·32	14·43
65·66	65·66	14·35	14·55
65·90	65·92	13·92	14·07
65·08	65·02	13·45	13·47
65·58	65·58	14·43	14·52
		12·33	12·40
		16·65	16·57
Mean 65·94	65·94	15·00	14·995

The much better precision of the wet coal determinations was due to the greater amount of water (3 g as against 0·3 g in the 'air-dried') which made the variation in the blank negligible.

From the results shown in *Tables 1* and *2* it was concluded that in the temperature range 90° to 140°C, for drying periods up to 3 hours, the loss of weight of coal dried in nitrogen could be taken as the weight of water evolved. This conclusion is in agreement with that of G. M. BROWN[2] in work done on brown coals for the Victorian sub-committee of the Coal and Coke Sectional Committee of the Standards Association of Australia.

The amounts of carbon dioxide given off were small when the coal was dried in nitrogen and showed a slight increase with time and temperature. Since the water alone was equal to the loss of weight, nitrogen must be adsorbed on the surface of the coal in amounts approximately equal to the carbon dioxide evolved for these temperatures and times, the pickup of moisture by the coal in the Quick-fit dishes between removal from the oven and weighing being negligible. There was no significant difference between the amounts of carbon dioxide (per gramme of dry coal) for the wet and 'air-dried' samples given in *Tables 1* and *2* but the 'air-dried' series were not samples of the same coals as those used in the wet series.

For the coal dried in air the carbon dioxide and $G - L$ were much greater than when nitrogen was used and showed a marked increase with time and temperature. Here the much larger amounts of carbon dioxide and water evolved were apparently more than balanced by the addition of air or oxygen to the coal itself so that the net result was a smaller loss than when a sample of the same coal was dried in nitrogen.

Table 3. Means of duplicate determinations

% carbon dioxide on dry weight—140°C—nitrogen			
Sample	*Wet*	*'Air-dried'*	*Time of drying h*
1	0·28	0·28	2
2	0·245	0·24	2
3	0·18	0·17	2
4	0·32	0·305	2
5	0·31	0·335	3
6	0·35	0·36	3
7	0·28	0·28	2
8	0·235	0·265	2
Mean	0·275	0·279	

The final experiment in this series gave further information on the relative amounts of carbon dioxide given off in nitrogen drying from fresh wet coal and a sample of the same coal which had been 'air-dried' by the routine procedure. The details given in *Table 3* show that equal amounts of carbon dioxide were evolved from wet and 'air-dried' samples of the same coal.

Possibility of including water derived from combustible hydrogen in loss when coal is dried in nitrogen

In order to establish whether the water evolved when coal is dried in nitrogen contained any which was derived from combustible hydrogen, calorific values were determined on wet coal and on the same coal dried in nitrogen for 3 hours at 110° and 140°C respectively, such values being calculated on the 'wet' (as-received) basis.

At these temperatures about 0·1 per cent of carbon dioxide was evolved. If this were derived from combustible carbon it is probable that the water included some derived from hydrogen in the coal substance. 0·1 per cent of water coming from this source would cause a drop in the calorific value of about 6 B.t.u./lb (heat of combustion of hydrogen to liquid $\simeq$ 34 cal/mg) and 0·1 per cent carbon dioxide would produce a further loss of approximately 4·5 B.t.u./lb (heat of combustion of carbon $\simeq$ 8 cal/mg). Therefore, a minimum loss of 10 B.t.u./lb could be expected if the carbon dioxide and 0·1 per cent of the water evolved were from combustible carbon and hydrogen respectively.

The experimental procedure which is given in detail was designed to eliminate all bias so that a fair comparison could be made between the determinations on the wet and the dried coal. After opening the bottle containing the sample and mixing thoroughly, 3·5 to 4·0 g of wet coal were placed as quickly as possible into each of two pairs of tared moisture dishes, lids were replaced and the dishes re-weighed. To prevent oxidation on standing the two to be used for calorific value (as-received) determinations were fitted with two-holed rubber stoppers through which nitrogen was passed for 5 minutes and the holes then sealed. (This resulted in a loss of about 1 per cent in weight.) The other two were placed in the oven at the required temperature and nitrogen was passed through the dishes for the duration of the test.

When the oven drying was finished the four calorific value determinations were made. The samples were left in the closed moisture dishes until needed for this determination when they were transferred completely to the platinum firing crucible, the original wet weight being taken for the calculation. The order of sampling, weighing and firing was alternated between the wet and dry tests from day to day so that any bias due to position would be cancelled. The as-received coal burnt contained about 2·5 g of water not present in the dry coal and it was found that there was a highly significant difference in the water equivalent of the calorimeter when 1 ml and 3·5 ml of water, respectively, were placed in the bomb. About 2·5 ml of water were therefore added to the base of the bomb for the dried coals in addition to the 1 ml normally added and the water equivalent with this amount of water was used for all determinations. (Some of this water was actually mixed with the dry coal to prevent spattering but the total amount of water in the bomb was the same for wet and dry coal.)

The means of duplicate determinations on 6 different coals are given in *Table 4*.

The differences between the means of the determination on the as-received and dried coal approximated to zero and there was no significant difference

between the variances of $W - D$ for the two temperatures. They may be combined therefore to give a better estimate of the precision. For significance at the 5 per cent level a difference of 2·5 is required, which means that in 19 out of 20 such experiments a constant difference of 2·5 B.t.u./lb would be apparent.

Table 4. Calorific values of wet (as-received) coal compared with those (converted to as-received basis) of samples of same coals after drying in nitrogen—means of duplicates (B.t.u./lb, $-\frac{1}{32}$ in. coal)

No.	*Wet (W)*	*Dry (D) (Nitrogen—110°C—3 h)*	*W − D*	*Wet (W)*	*Dry (D) (Nitrogen—140°C—3 h)*	*W − D*
1	3853	3857	−4	3847	3841	+6
2	3884	3880·5	+3·5	3809	3816·5	−7·5
3	3980	3984	−4	3974	3975·5	−1·5
4	3855	3850·5	+4·5	3858·5	3856·5	+2·0
5	3929	3927	+2	3934	3933	+1
6	3907	3908·5	−1·5	3910	3912·5	−2·5
Mean	3901·4	3901·3	+0·1	3888·8	3889·2	−0·4

It could be assumed on this evidence that no measurable oxidation was occurring at these temperatures and times of heating provided that the latent heat of vaporization of the water in burning coal has a normal value. If it is higher than normal, as predicted from the lower vapour pressure of the moisture in coal, then the as-received will be lower by the amount of the excess latent heat. In this case, it would have to be assumed that oxidation must be taking place in the nitrogen oven exactly equal to this effect, which should produce a fall of about 10 B.t.u./lb for the as-received coals, estimated from the curve given by F. A. BULL[3].

To produce conditions which would demonstrate the oxidation of the drying coal (if such were occurring) over and above this value, the last experiment was repeated with the following variations. Determinations of calorific value were made on:

(*1*) the as-received coal immediately
(*2*) the coal after drying in nitrogen at laboratory temperature for 20 hours
(*3*) the coal after drying in nitrogen at 140°C for 20 hours.

All samples were weighed in moisture dishes and each transferred to the firing crucible immediately prior to the calorific value determination as before, the order of sampling, weighing, etc., being cyclic. The nitrogen coming out of the oven after passing over pair (*3*) was passed through Anhydrone and Carbosorb and then over pair (*2*) outside the oven; 55 to 60 per cent of weight was lost by the latter pair. No carbon dioxide is given off by coal dried in nitrogen at laboratory temperature, but a further 0·1 to 0·15 per cent was evolved by the oven-dried pair and 0·2 to 0·3 per cent more water during the 17 additional drying hours.

No measurable oxidation occurred for periods of up to three days in fresh raw coal which was kept at a temperature of 20°C out of contact with the air,

except during initial sampling, sieving, etc. Any difference in calorific value between the first and the second series would therefore be produced by the difference in the excess latent heat effect for their different residual moistures.

The means of duplicate determinations on four different coals are given in *Table 5.*

Table 5. Comparison of calorific values (as-received basis) of as-received coal and of samples of same coal dried in nitrogen for 20 hours at 20° and 140°C respectively (B.t.u./lb, $-\frac{1}{72}$ in., means of duplicates)

Immediately on as-received coal		*Dried in nitrogen 20°C—20 h*	*Dried in nitrogen 140°C—20 h*	*Differences* 1 − 2	1 − 3
No. 1	3843	3837·5	3838·5	+5·5	+ 4·5
No. 2	3855	3854·5	3848·5	+0·5	+ 6·5
No. 3	3970	3972·5	3972·5	−2·5	− 2·5
No. 4	4012	4006·5	4023	+5·5	−11·0
Mean	3920·0	3917·8	3920·6	+2·2	− 0·6

The difference between the means of the wet and oven-dried coals again approximated to zero; thus conditions favouring further oxidation (or decomposition) failed to produce any difference in these mean calorific values, nor did the coal dried at 20°C have a higher calorific value than the wet coal by virtue of its much lower moisture content, together with the postulated excess latent heat effect. One must conclude, therefore, that no measurable oxidation was occurring under these conditions; hence, neither the carbon dioxide nor any of the water evolved was derived from combustible matter; and, lastly, there was no evidence that the water expelled had an abnormal heat of vaporization.

Table 6. Calorific values (air-dried basis) of 'air-dried' coal after prolonged drying in nitrogen at 20° and 140°C, respectively—B.t.u./lb

Immediately on 'air-dried' coal		*Dried in nitrogen 20°C—20 h*	*Dried in nitrogen 140°C—20 h*	*Differences* 1 − 2	1 − 3
No. 1	9298	9296·5	9221	+ 1·5	+77
No. 2	8439	8434	8376	+ 5	+63
No. 3	9631	9618	9572	+13	+59
Mean	9122·7	9116·2	9056	+6·5	+67

For significant difference of means (last column) at the 1 per cent level $d > 54$ B.t.u./lb.

The last experiment was repeated with coal which had been exposed to the atmosphere for 48 hours (− 72 mesh B.S. sieve). The results given in *Table 6* show that significant degradation is occurring with 'air-dried' coal subsequently dried for 20 h at 140°C in nitrogen. However, the products of this oxidation must be non-volatile, as equal amounts of carbon dioxide were given off from wet and 'air-dried' samples of the same coal, and it has

already been demonstrated that the carbon dioxide evolved from wet coal produced no loss in the heat of combustion.

Another series of determinations of calorific value was made in which the coal was burnt in the calorimeter after it had been dried in nitrogen at 140°C, so that the results referred to the dry basis. Duplicate determinations were made on eight coals as follows:

(*1*) Samples unexposed to the air except during initial crushing and sieving
(*2*) Samples of the same coals after 'air-drying' at laboratory temperature for 48 hours prior to the nitrogen oven drying.

These calorific values were compared with those obtained by the routine procedure of burning the coal in the 'air-dried' condition and converting to the dry basis using the results of separate moisture determinations. At the beginning of an experiment, duplicate determinations were made immediately on each coal, as-received, together with an air-oven moisture.

The data are summarized in *Table 7*.

Table 7. Calorific values (dry basis). Means of duplicate determinations on 8 coals (B.t.u./lb)

	Coarse coals unexposed to atmosphere ($-\frac{1}{32}$ *in.*)	*The same coals after exposure to atmosphere for 48 h* (-72 *mesh B.S.*)	
	Oven dried in nitrogen—140°C—3 h	*Oven dried in nitrogen—140°C—2 h*	*'Air-dried' coal in nitrogen*
C.V. B.t.u./lb	(*A*) 11 373	(*B*) 11 301	(*C*) 11 187 (*Air oven, 110°C*) (*D*) 11 321 (*Nitrogen oven, 140°C*)
% Loss, nitrogen oven, 140°C	66·763	17·564	
% Loss, air oven, 110°C	66·199	16·566	

Mean 3 781 B.t.u./lb, as received.

C − *D* represented the error in the calculated calorific value (dry basis) in the determination on 'air-dried' coal due to a too low moisture determination in the air oven at 110°C.

D − *B* showed the amount of oxidation occurring in the 'air-dried' coal while drying in nitrogen at 140°C for 2 hours, and *A* − *D* the oxidation due to exposure to the atmosphere for 48 hours.

An interesting point arising from this experiment provided a further indication that the wet and 'air-dried' coal may not be dried to the same extent at 110°C. A comparison of their moistures in the air oven at 110°C with those of nitrogen at 140°C gave $N_{140} - Air_{110} = 0{\cdot}564$ per cent for as-received and 1·00 per cent for 'air-dried' coal. Converting these to the dry basis, they become 1·70 and 1·21 per cent, respectively, a difference of 0·49 which was significant at the 2½ per cent level. Furthermore, if the calorific value, dry basis, was calculated from the mean as-received, using the air-oven moisture to obtain the dry weight, the value obtained, 11 187 B.t.u./lb, was identical with that of the mean routine determination, the deterioration of the 'air-dried' coal during exposure being balanced by the above effect.

The difference in the value of $N_{140} - Air_{110}$ for the wet and 'air-dried' coals was confirmed by the following experiment. Loss of weight was determined on six fresh wet coals ($-\frac{1}{4}$ in.) and the same coals after air drying by the routine method ($-$ 72 mesh B.S.):

(*1*) in the air oven at 110°C to constant weight
(*2*) in nitrogen at 140°C for 3 hours.

The order of sampling and weighing was alternated between the air and nitrogen oven dishes to cancel real differences in moisture occurring during this operation. *Table 8* shows the relationship $N_{140} - Air_{110}$ for the two types of sample, the difference in its value being significant at the 1 per cent level for 5 degrees of freedom.

It is worth while to note here that this difference is possibly associated with the freshness of the coal rather than its particle size. Three composite samples of as-received coal (64 to 65 per cent moisture) which had been stored for a month in a tin that was opened daily to add increments, with no precautions taken to exclude air, gave the same value for $N_{140} - Air_{110}$ for the wet and 'air-dried' samples.

Table 8. Value of the relationship $N_{140} - Air_{110}$ for wet and 'air-dried' samples of the same coals

No.	*% dry wt at 140°C—nitrogen*		*Difference*
	Wet samples	*'Air-dried' samples*	
1	1·84	1·24	0·60
2	2·17	1·32	0·85
3	1·43	1·24	0·19
4	1·63	1·37	0·26
5	1·81	1·36	0·45
6	1·76	1·47	0·29
Mean	1·77	1·33	0·44

Significance $P = 0{\cdot}01$, $d > 0{\cdot}41$.

The difference may be due to a different balance between volatile and non-volatile oxidation products in the wet and 'air-dried' samples in the air oven, but could be due to a greater amount of residual moisture in the fresh raw coal after drying at 110°C. The latter explanation is based on the weight loss/temperature curves in *Figure 3* which suggest that the raw and 'air dried' coals are not equally dry till a temperature of at least 140°C is reached.

DISCUSSION

The determination of the total water content of coal is necessary for its accurate analysis, but for its use as a fuel, the gross and net calorific values as-received, are of prime importance. For the determination of these, the total moisture (as distinct from the total water formed in combustion) is not necessary.

The gross calorific value is the number of heat units liberated when unit mass of the fuel is burnt under standard conditions and the water produced by the combustion is condensed. The net calorific value (N) is the gross value less the amount of heat lost in the vaporization of the water produced by combustion.

At Yallourn, the formula used to obtain N from the gross dry calorific value (G) is

$$N = \frac{100 - M}{100}\left\{ G - L\left(\frac{M}{100 - M} + \frac{9H}{100}\right)\right\}$$

where M is the percentage moisture of the coal 'as received', L the latent heat of water and H the percentage hydrogen in the dry coal.

Too low a value of M also alters the value of the 'gross dry' and the hydrogen value. If the moisture determination is altered to give a much higher M, G will increase and H decrease by exactly proportional amounts, so that N will remain unaltered. Hence any error in M, due to inadequate methods for moisture determination, is automatically corrected by the formula. This fact is subject to the one important condition, that the moisture on the 'as-received' coal is consistent with the moisture determination associated with the sample for analysis. In other words, after oven-drying both, the amount of water left in them is the same.

It has been shown that this condition is not fulfilled for Yallourn coal when air oven (110°C) moistures are used, due to the different properties of the wet and 'air-dried' samples, producing the same effect as a difference in the residual water content of about 0·45 per cent on the dry weight. This would give rise to an error of + 50 B.t.u./lb in the gross dry calorific value. In Yallourn coal, however, there is a compensating negative error produced by oxidation of the 'air-dried' sample during exposure to the atmosphere.

It is considered possible that the moisture-retaining properties of this brown coal alter with its age* and that differences in the rates of drying in nitrogen of wet and 'air-dried' coal up to 140°C are related to its age rather than to its particle size or total moisture content. More evidence on this point is needed, but caution should be exercised in comparing and interpreting results on coals that have been stored for different periods unless special precautions have been taken which: (*1*) prevent changes in properties between mining and testing, and (*2*) prevent or compensate for those occurring during tests.

Finally, it may be stated that the very different properties of the 'as-received' and 'air-dried' coal make the use of the latter undesirable unless it has been ascertained that the errors introduced by this 'two-stage' drying are compensatory. If the indeterminate end point of the method of thermal drying in nitrogen is general for all brown coals, it detracts from its value as a standard method in the determination of moisture.

* 'Age' being used in the sense of time elapsed between mining and testing the coal.

CONCLUSIONS

This work has led to the following conclusions:

(*1*) All the moisture in the coal is not expelled by heating to constant weight in air at 110°C and the loss of weight so obtained is at least 0·8 per cent lower than the moisture content (66 per cent).

(*2*) No definite end point to the drying of coal in nitrogen has been obtained. The coal continues to lose weight with increasing temperature and drying time for temperatures up to 180°C and periods up to 48 hours. The possibility that this continued loss is due to coal being carried by the current of nitrogen has been eliminated.

(*3*) The loss of weight of coal dried in nitrogen in the temperature range 90° to 140°C for 3 hour periods is equal to the weight of the water evolved.

(*4*) No oxidation of fresh raw coal occurs while drying in nitrogen at 140°C for periods up to 20 hours but significant degradation occurs in coal which has been air-dried prior to the nitrogen-oven drying. The products of this oxidation are non-volatile.

(*5*) Some carbon dioxide is evolved during thermal drying in nitrogen which increases slightly with time and temperature but is independent of the particle size or the exposure to air of the sample prior to oven drying. Nitrogen is adsorbed on the coal in approximately equal amounts to the carbon dioxide evolved.

(*6*) There is no evidence that the water expelled by drying in nitrogen at 140°C for periods up to 20 hours has an abnormal latent heat of vaporization.

(*7*) The weight loss/temperature curves for coal drying in nitrogen show that the rates of drying are different for wet and 'air-dried' samples of the same coal for temperatures up to 140°C.

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The Standardization of Methods of Analysis of Coal and Coke

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THE careful investigation of the standard method of determining carbon and hydrogen in coal and coke by members of the appropriate British Standards Committee (45/8) has led to a new specification (*B.S. 1016*, Parts 6 and 7. British Standards Institution: London, 1958) which must, if rigidly observed, increase the accuracy of these determinations. It should, however, be pointed out that the standard is aimed at the formulation of an accurate method for one analysis and that, although the packing of the combustion tube will undoubtedly serve for a number of determinations, it is not the aim of the specification to say exactly how many, since this must vary from one laboratory to another with the degree of care taken with the first packing.

It was inevitable, also, that special consideration should be given to the need for speed in routine laboratories and this has led to the standardization of a 'high-temperature' alternative method which allows a considerably larger number of analyses to be completed in a working day. At an early stage it was demonstrated by L. J. EDGCOMBE [*Fuel, Lond.* 34 (1955) 185] that there was no significant difference in the results obtained by the two methods, although the variance in the case of the Liebig method was slightly lower than in the high-temperature method.

At the 1953 Conference (I.S.O./TC 27) several delegates, particularly those of India, had expressed concern at the possibility of the escape of oxides of nitrogen from the Liebig combustion tube which, by oxidation to peroxide and absorption in water or carbon dioxide-absorption vessels, could appreciably affect the result for carbon, and to a lesser degree that for hydrogen. It was therefore arranged for several members of the Committee 45/8 to make investigations, in order to be quite sure of the true facts. These investigations have shown that the escape of oxides of nitrogen can occur, and can increase the apparent percentage of carbon by as much as 0·2 per cent in the analysis of coal, and the percentage of hydrogen by about 0·05 per cent or less. In order to guard against any possible errors it has been decided to introduce a guard tube containing manganese dioxide (and Anhydrone) between the moisture-absorption vessel and the carbon dioxide-absorption vessel after the micro-method of R. BELCHER and G. INGRAM [*Analyt. chim Acta* 4 (1950) 118, 401]. Slight modifications only have been necessary in order to suit the larger scale of the Liebig method and to standardize the reagent. This guard tube is now included in the new specification.

In examining this problem R. A. MOTT and H. C. WILKINSON [*Fuel, Lond.* 37 (1958) 62] have concluded that the escape of oxides of nitrogen from either the Liebig or the high-temperature method is negligible, but that the accuracy of the determination may be affected, after some 40 determinations with the

same tube, by the escape of oxides of sulphur. M. P. MENDOZA, however, [*Fuel, Lond.* 37 (1958) 409] has shown that, if nitric oxide is passed into a Liebig tube in the amount likely to be found in a C/H determination, almost half may escape and contaminate the absorption tubes as nitrogen dioxide, rather more than half of the amount escaping being found in the carbon dioxide tube. When the manganese dioxide tube was inserted in the train no nitrogen dioxide reached the carbon dioxide-absorption tube. When he then analysed a number of coals and cokes he found that the actual amounts of nitrogen dioxide absorbed in the guard tube were somewhat variable but that the mean indicated an error in the carbon value of + 0·24 per cent. Analysis of the manganese dioxide before and after use also demonstrated that oxides of sulphur had not escaped and that the gain in weight of the tube was due wholly to nitrate.

In a similar investigation A. H. EDWARDS [*Fuel, Lond.* 37 (1958) 415] has obtained a similar value to that obtained by Mendoza of + 0·17 per cent in the carbon value. Also, by the analysis of the manganese dioxide reagent after use, he has confirmed that oxides of sulphur do not escape in the Liebig method. Edwards has also examined the high-temperature method and confirms Mott and Wilkinson in that the amount of nitrogen dioxide which escapes in this method is negligible: the actual amount would affect the carbon value by 0·04 per cent only. In a later series of Liebig determinations using a guard tube, the absence of oxides of sulphur in the reagent after 32 analyses was demonstrated.

These new investigations confirm the wisdom of having a guard tube in the Liebig absorption train, and such is now included in the new B.S. specification. The small residual error in the hydrogen value is considered to be within the experimental error. It is also considered that the guard tube is not necessary in the case of the high-temperature method. It is repeated that the standard method laid down relates to fresh combustion tubes and that it is the additional duty of any analyst who makes repeat determinations with the same tube to ensure that it remains in effective condition, particularly as regards the lead chromate packing and the silver gauze.

The Determination of Carbon and Hydrogen in Coal and Coke by the Liebig Method: Elimination of the Errors due to the Formation of Nitrogen Dioxide

M. P. MENDOZA

The probable errors in both carbon and hydrogen values for coal and coke determined by the B.S. Liebig method due to nitrogen dioxide absorption have been assessed. Better carbon values may be obtained by absorbing the oxides of nitrogen in granular manganese dioxide. An empirical correction for hydrogen is suggested.

IT has been known for a long time that when nitrogenous compounds are burnt in oxygen, nitric acid is among the products. On cooling in the presence of oxygen, nitric oxide reacts with it forming nitrogen dioxide. The reaction is reversible and the composition of the equilibrium mixture dependent on the temperature. At temperatures above 620°C there is no nitrogen dioxide[1]; below 130°C, conversion of nitric oxide to nitrogen dioxide is complete.

In the Liebig method for the determination of carbon and hydrogen in coal and coke approximately 200 mg of the sample is burnt in a stream of oxygen, the resulting water and carbon dioxide being absorbed and weighed in U-tubes containing dried magnesium perchlorate (Anhydrone) and soda–lime respectively. The gaseous products of combustion pass through a packed tube, first over copper oxide at 775° to 800°C to complete their oxidation, then over lead chromate at 575° to 600°C to remove oxides of sulphur and arsenic and finally over a hot metallic gauze the temperature of which is 550°C at the inner (hotter) end and about 200°C at the other. Silver is specified for this gauze by the British Standards Institution[2] whereas the Fuel Research Board[3] recommends copper.

In the B.S. Liebig method, some of the nitric oxide is oxidized to nitrogen dioxide in the combustion tube by the excess of oxygen present and is absorbed by the packing, in particular, by the silver gauze which is maintained below 620°C. This was shown to be so by confirming with the brucine test the presence of nitrate in the water washings of silver gauze rolls which had been used for coal analysis.

Any nitrogen dioxide, or any nitric oxide which would be converted by the oxygen to nitrogen dioxide, leaving the combustion tube is most likely

to be absorbed in the U-tubes containing Anhydrone and soda–lime. There, it would be weighed together with the water and carbon dioxide, thus producing erroneously high values for carbon and hydrogen.

MAGNITUDE OF THE ERRORS

To obtain some indication of the magnitude of the errors likely to be incurred when coal and coke is analysed using either silver or copper gauze in the combustion tube, 4 ml portions of nitric oxide were injected each over a period of 30 minutes into the oxygen stream of otherwise 'blank' determinations. After sweeping out for a further 90 minutes, the increases in weight of the U-tubes containing Anhydrone and soda–lime were determined. 4 ml of nitric oxide, equivalent to 8 mg of nitrogen dioxide, approximates to what would be formed from the quantitative oxidation of the nitrogen in 200 mg of material of 1·3 per cent nitrogen content; 30 minutes is the time normally taken to complete the combustion of a sample.

Table 1. Increase in weight of U*-tubes containing Anhydrone and soda–lime for 4 ml nitric oxide injected*

Silver gauze			*Copper gauze*		
Test No.	*Anhydrone tube mg*	*Soda–lime tube mg*	*Test No.*	*Anhydrone tube mg*	*Soda–lime tube mg*
1	0·8	2·3	*1*	1·4	3·2
2	0·7	1·0	*2*	1·5	1·6
3	0·9	0·4	*3*	0·9	1·4
4	1·2	1·6	*4*	1·3	1·8
	Mean 0·9 ≡ 0·05% H	*Mean* 1·3 ≡ 0·18% C		*Mean* 1·3 ≡ 0·07% H	*Mean* 2·0 ≡ 0·27% C

The results in *Table 1* show that appreciable quantities of nitrogen dioxide were absorbed in both U-tubes. Similar amounts absorbed during determinations would produce carbon and hydrogen values high by approximately 0·2 and 0·05 per cent respectively. Under the conditions prevailing, silver gauze, recommended by the British Standards Institution, tended to be rather more efficient than copper in retaining nitrogen dioxide.

PREVENTION OF ERRORS IN THE CARBON VALUE

R. BELCHER and G. INGRAM[4] have described a very convenient method for overcoming the error in the carbon value when working on the micro scale. These authors remove nitrogen dioxide in an absorption vessel containing granular manganese dioxide followed by Anhydrone, placed after the absorption tube for water and before that for carbon dioxide. The design of the vessel is such that there is sufficient 'dead space' in which all the nitric oxide has time to oxidize to nitrogen dioxide before coming into contact with the manganese dioxide. Baffled vessels of the size and type recommended by these authors for use with their rapid micro method for carbon and hydrogen determination[5] were used for this investigation. The reagent was prepared by the following method outlined by Belcher[6].

PREPARATION OF THE MANGANESE DIOXIDE GRANULES

Hydrated manganese dioxide was prepared by the dropwise addition of a slight excess of ammonia to a hot solution containing manganese sulphate and an excess of a persulphate. If the precipitate produced was slightly brownish it was completely oxidized by the addition of a little hydrogen peroxide. When the precipitate had settled, the supernatant liquid was decanted and the residual mud heated with an equal volume of 10 per cent (v/v) sulphuric acid for 30 minutes whilst stirring frequently. The purified precipitate was washed several times by decantation through a Büchner funnel with hot distilled water until the washings were no longer acid to litmus. The precipitate was then transferred to the Büchner funnel and drained, then heated in an oven at 150°C until visibly dry. The hard compact cake so produced was gently crushed and that fraction retained which passed through a 10 mesh but remained on a 14 mesh B.S. test sieve. It was not found possible to work up the fines into granules by damping and drying.

ANALYSIS OF STANDARD COMPOUNDS

Sucrose, dibenzyl disulphide and phenacetin were analysed in order to confirm: (*i*) that complete combustion was being effected, (*ii*) that the nitrogen dioxide absorbers did not also absorb carbon dioxide, (*iii*) that no sulphur oxides escaped from the combustion tube, and (*iv*) that one manganese dioxide absorber would be sufficient to remove all oxides of nitrogen remaining after absorption of the water when coal or coke is analysed. The combustion tubes had been used regularly for coal or coke during several weeks prior to the determinations and the results are shown in *Table 2*.

Table 2. Analyses of synthetic compounds

Compound	*% Hydrogen*		*Increase in weight of* MnO_2 *tube (mg)*		*% Carbon*	
	Theoretical	*Observed*	1	2	*Theoretical*	*Observed*
Sucrose $C_{12}H_{22}O_{11}$	6·48	6·43 6·50	0·0 0·0	— —	42·10	42·13 42·20
Dibenzyl disulphide $C_{14}H_{14}S_2$ S = 26·0%	5·73	5·73 5·84	0·2 0·0	— —	68·25	68·31 68·26
Phenacetin $C_{10}H_{13}O_2N$ N = 7·8%	7·31	7·41 7·69*	2·5 6·5	−0·3 0·4	67·02	66·98 66·96

* Sample caught fire in combustion tube apparently increasing nitrogen dioxide formation.

Sucrose and dibenzyl disulphide contain no nitrogen and for these, one manganese dioxide absorber was interposed between the U-tubes containing Anhydrone and soda–lime. Any apparent change in the weight of this absorber was within the limit of accuracy of the balance used, ± 0·2 mg. For these two compounds carbon and hydrogen values in satisfactory agreement with theoretical were obtained.

Phenacetin contains considerably more nitrogen than coal or coke and in this case two absorbers connected in series were included. The weight of the first absorber increased markedly but there was no appreciable change in the weight of the second. Hydrogen values were higher than those calculated but good carbon values were obtained.

ANALYSIS OF COAL AND COKE

A series of coals and cokes was analysed in duplicate. One determination was carried out by the B.S. method but, in the other, an absorber for nitrogen dioxide was inserted. The amounts of nitrogen dioxide removed were somewhat variable (*Table 3*) but the average amount would cause an error of + 0·24 per cent in the reported carbon content. The inclusion of the absorber

Table 3. Carbon values for coals and cokes with and without the removal of oxides of nitrogen

Lab. No.	% C (NO_2 *removed*) C_1	*Weight of* NO_2 *absorbed mg*	'% C' *from* $CO_2 + NO_2$	% C *by B.S. method* C_2	$C_2 - C_1$ %
10881	—	—	—	74·12	
	73·90	2·2	74·19	—	0·22
10965	—	—	—	57·86	
	57·57	2·5	57·91	—	0·29
*11055**	—	—	—	81·07	
	80·96	1·3	81·13	—	0·11
11058	—	—	—	68·04	
	67·82	1·1	67·97	—	0·22
11074	—	—	—	76·68	
	76·60	1·9	76·86	—	0·08
11085	—	—	—	59·73	
	59·56	1·8	59·80	—	0·17
*11106**	—	—	—	82·69	
	82·49	2·3	82·81	—	0·20
11107	—	—	—	70·36	
	70·19	0·8	70·30	—	0·17
	Mean	1·7 (≡ 0·24% C)			*Mean* 0·18%C

* Coke

containing manganese dioxide lowered the carbon value by an average of 0·18 per cent only, but a significance test showed that statistically the difference between 0·18 per cent and 0·24 per cent was not significant at the 5 per cent level.

EXAMINATION OF THE MANGANESE DIOXIDE

The manganese dioxide from the absorbers used for the tests was combined, ground and its total sulphur content was determined. The value obtained was identical with that of the unused material, being 0·68 per cent in each case.

DISCUSSION OF RESULTS

The agreement of the determined values for sucrose with theoretical and the absence of any increase in weight of the absorber for nitrogen dioxide show that there was no absorption of carbon dioxide by the manganese dioxide. These results also confirmed that complete combustion and quantitative absorption of the water and carbon dioxide were being effected.

When dibenzyl disulphide was analysed, no appreciable change in the weight of the absorber containing manganese dioxide was noted. Also, the total sulphur content of the manganese dioxide from the absorbers after all the tests showed no increase over that of the original material. These observations and the fact that satisfactory carbon and hydrogen values were obtained indicate that even when a substance containing 26 per cent of sulphur was burnt, the oxides of sulphur were retained by the normal packing of the combustion tube.

The analyses of phenacetin show that when a compound containing considerably more nitrogen (7·8 per cent) than coal (*ca.* 1·5 per cent) was analysed, one absorber was sufficient to retain all the oxides of nitrogen passing into it thus enabling correct carbon values to be obtained. However, presumably because of the absorption of nitrogen dioxide with the water, the hydrogen values for phenacetin were in excess of its theoretical hydrogen content.

In the case of coals and cokes (*Table 3*), if the weight of the nitrogen dioxide collected is added to the corresponding weight of carbon dioxide, the 'carbon' value obtained is in good agreement with its duplicate determined by the standard procedure. It is apparent therefore that carbon values for coals and cokes, obtained by a Liebig method which ignores the presence of nitrogen dioxide in the gases leaving the combustion tube, are approximately 0·2 per cent high.

The results of the preliminary experiments with nitric oxide indicate that only by removing oxides of nitrogen prior to the absorption of the water can correct hydrogen values be obtained. However, using manganese dioxide, attempts to remove oxides of nitrogen at this stage failed. The reagent also absorbs water vapour which is desorbed only slowly by sweeping with dry oxygen even at 160°C. Since, when the coals and cokes were analysed, the weights of nitrogen dioxide collected prior to the absorption of carbon dioxide were similar to the increase in weight of the soda–lime tube in the preliminary experiments (*Table 1*), it seems reasonable to assume that the amounts of nitrogen dioxide leaving the combustion tube were comparable in both instances. The hydrogen values obtained for coals, therefore, have in all probability a positive error of approximately 0·05 per cent (equivalent to 0·9 mg 'water') for which an empirical correction may be made if desired.

The absorption tube and its packing, designed by Belcher and Ingram[4] for use in the rapid micro determination of carbon, has been found to be applicable without modification to the Liebig macro method. From the point of view of absorber efficiency, it is probable that the potentially greater weight

of oxides of nitrogen emitted in the macro method is more than counterbalanced by the much slower flow rate of oxygen, i.e. 12 ml per minute compared with 50 ml per minute in the micro method.

CONCLUSIONS

The packing of the Liebig combustion tubes employed in the determination of carbon and hydrogen in coal and coke does not retain all the oxides of nitrogen which may be formed[1] on combustion of the sample. Using the present B.S. method, carbon values are on the average about 0·2 per cent high. This error may be eliminated by removing the nitrogen dioxide with manganese dioxide by the method of Belcher and Ingram before absorbing the carbon dioxide. Although no method for eliminating the error in the hydrogen value has been found, there is indirect evidence that its magnitude is about + 0·05 per cent.

This work, carried out in the Analytical Section of the Chemistry Department of the B.C.U.R.A., arose from the deliberations of the British Standards Institution Sub-committee SFE/45/8 during the revision of B.S. 1016: 1942 '*British Standard Methods for the Analysis and Testing of Coal and Coke*'. *The author is indebted to Dr R. Belcher (The University, Birmingham) for helpful discussions, to J. Jordan and D. L. Ward who performed some of the determinations, and to the British Coal Utilisation Research Association for permission to publish this paper.*

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Evolution of Oxides of Nitrogen and of Sulphur during the Determination of Carbon and Hydrogen in Coal

A. H. EDWARDS

The paper describes an investigation into the evolution of oxides of nitrogen and sulphur in the Liebig method for the determination of carbon and hydrogen in coal. It is demonstrated that the oxides of sulphur produced during the combustion are completely absorbed in a properly packed Liebig tube and that oxides of nitrogen are evolved in quantities sufficient, unless removed, to cause an error of approximately 0·2 per cent in the carbon determination. The effectiveness of manganese dioxide in removing these oxides of nitrogen is confirmed. It is shown that only traces of oxides of nitrogen are evolved in the Sheffield High Temperature method.

COMBUSTION of coal can give rise to the formation of oxides of sulphur and of nitrogen in addition to those of carbon and hydrogen. Evolution of these oxides of sulphur and nitrogen from the combustion tube during a determination of the carbon and hydrogen in coal can lead to errors in the determination unless steps are taken to remove them. The combustion tube used in the Liebig method[1, 2] contains a packing of lead chromate for the removal of oxides of sulphur but in the past no specific precaution has been taken to deal with any oxides of nitrogen formed during combustion.

At the third meeting of the I.S.O. Technical Committee on Solid Mineral Fuels, held in London in 1953, it was suggested that a Liebig combustion results in the formation of oxides of nitrogen and that these are evolved in quantities sufficient to introduce appreciable errors in the carbon determination. The present investigation originates from these I.S.O. discussions and has been designed to demonstrate the evolution of oxides of nitrogen, to determine the magnitude of their effect on both carbon and hydrogen determinations, and to suggest a method of eliminating the errors so caused. Cognizance has also been taken of the recently published assertion of R. A. MOTT and H. C. WILKINSON[3] that, contrary to general belief, oxides of sulphur escape from the combustion tube during a Liebig combustion.

The work has been confined in the main to the Liebig method, but some attention has been paid to the High Temperature method originated by R. BELCHER and C. E. SPOONER[4] and further developed by the Midland Coke Research Station.

OXIDES OF NITROGEN IN THE LIEBIG METHOD

Quantitative estimation of oxides of nitrogen and sulphur

Six coals, with sulphur and nitrogen contents ranging from 0·6 to 5·3 per cent

and 1·6 to 2·0 per cent respectively, were used in two parallel series of combustions. In each series, combustion of 0·2 g of each coal was carried out in a correctly packed Liebig tube, the products of combustion being passed through a sintered glass bubbler of the type used for the determination of sulphur and chlorine by the High Temperature method. In the first series, the bubbler contained a 1 per cent solution of hydrogen peroxide in water, an arrangement which has been shown[5] to effect complete absorption of oxides of sulphur. In the second series, the reagent in the bubbler was a 1 per cent solution of hydrogen peroxide in 0·1N sulphuric acid, this being more effective than aqueous peroxide solution for absorption of oxides of nitrogen. The nitrate in both aqueous and acid solutions was determined colorimetrically with phenol–disulphonic acid. Sulphate in the aqueous solution was determined by precipitation under suitable conditions with barium chloride.

Table 1. Oxides of nitrogen and sulphur evolved during a Liebig carbon and hydrogen determination

Sample No.	*Sulphur (air-dried coal: per cent)*	*Nitrogen (air-dried coal: per cent)*	H_2O_2—*Water*				
			Nitrogen dioxide (per cent)		*Mean*	*Carbon equivalent*	*Sulphur (per cent)*
10713	2·56	1·8	0·75	0·75	0·75	0·20	*Nil*
10936	1·31	1·9	0·44	0·45	0·44	0·11	*Nil*
24325	0·58	2·0	0·95	0·95	0·95	0·25	*Nil*
24326	5·30	1·6	0·74	0·75	0·74	0·19	*Nil*
24327	5·25	1·8	0·61	0·61	0·61	0·16	*Nil*
24328	0·71	1·8	0·60	0·62	0·61	0·16	*Nil*

Sample No.	*Sulphur (air-dried coal: per cent)*	*Nitrogen (air-dried coal: per cent)*	H_2O_2—0·1N H_2SO_4					*Mean*	*Carbon equivalent*
			Nitrogen dioxide (per cent)						
10713	2·56	1·8	1·00	0·94	0·95			0·96	0·25
10936	1·31	1·9	0·85	0·86	0·96	0·94		0·90	0·23
24325	0·58	2·0	1·18		1·17			1·18	0·31
24326	5·30	1·6	1·04		1·04			1·04	0·27
24327	5·25	1·8	0·83		0·82			0·82	0·21
24328	0·71	1·8	0·95		0·98			0·96	0·25

The results obtained are given in *Table 1*. Contrary to the findings of Mott and Wilkinson[3], they confirm the general belief that oxides of sulphur produced during combustion are removed completely by the lead chromate packing in the standard Liebig combustion tube. They also confirm that oxides of nitrogen are produced and that they escape from the combustion tube. The experiments using acid peroxide solution establish that an error of about 0·25 per cent can be caused if these nitrogen oxides are allowed to be picked up in the carbon dioxide absorber and weighed as carbon dioxide. This is in excellent agreement with the average difference value (0·24 per cent) found by M. P. MENDOZA[6] when comparing carbon values obtained with and without removal of oxides of nitrogen prior to the absorption of carbon dioxide.

Removal of oxides of nitrogen

The formation of oxides of nitrogen during a Liebig combustion having been firmly established, methods for its removal during an actual determination were considered. In the laboratories of the Dutch State Mines[7] a tube is interposed containing silica gel impregnated with potassium dichromate and concentrated sulphuric acid (a guard of magnesium perchlorate is placed at each end of the U-tube). R. BELCHER and G. INGRAM[8] have used a tube filled with granular manganese dioxide followed by anhydrous magnesium perchlorate for the removal of nitrogen peroxide during the determination of carbon and hydrogen on the micro scale. Mendoza[6] used such tubes on the micro scale, but specially prepared the manganese dioxide packing, and found them perfectly satisfactory. The simplicity of the Belcher and Ingram manganese dioxide tube commends itself, and in order to verify its effectiveness as an absorber the reagent was removed and analysed for nitrate and sulphate after being used for a number of determinations.

The gain in weight of the manganese dioxide tube and the amount of nitrogen dioxide found later by analysis are given in *Table 2* together with the determined sulphur value in the manganese dioxide after use for 32 and 16 Liebig combustions.

Table 2. Nitrogen dioxide and sulphur in manganese dioxide

Experiment	*Nitrogen dioxide (mg)*		*Sulphur (mg)*
	Gain of MnO_2	*Determined in* MnO_2	*Determined in* MnO_2
After 32 determinations	32·9	37·0	0·036
After 16 determinations	19·0	16·8	0·030

Allowing for the errors involved in a large number of weighings, the gain in weight of the manganese dioxide tube corresponds within reasonable limits with the nitrogen dioxide determined colorimetrically as nitrate. The amount of sulphur found in the used manganese dioxide was practically nil when account was taken of the blank (0·005 per cent sulphur) on the unused material and it confirms the fact, proved earlier, that no oxides of sulphur escape from a properly packed Liebig tube.

During the determination of carbon on 29 coals reported below there were some indications that the Belcher and Ingram tubes were ineffective after eight determinations—they failed to gain in weight or even lost weight. They were replaced with 75 mm long, 10 mm diameter U-tubes with ground-in taps packed with granular manganese dioxide prepared according to the method of Mendoza, and having a guard of magnesium perchlorate at the outlet end. These proved to be quite as efficient and results obtained with them are given in *Table 3* (last seven results). On account of the larger amount of reagent they contain it is felt that they will have a much longer life than the Belcher and Ingram tubes.

Effect of manganese dioxide absorbers on carbon and hydrogen results

In order to determine the effect of manganese dioxide absorbers on carbon and hydrogen determinations tests were carried out on 29 coals with and

without such an absorber in the absorption train. Determinations were carried out in duplicate with occasional triplicates but only the mean results are recorded in *Table 3.*

The data reported have been examined statistically and analyses of variance have been carried out on all the carbon values obtained. The results using the

Table 3. Effect of manganese dioxide absorber on Liebig combustions

Sample No.	*Without* MnO_2 *tube*		*With* MnO_2 *tube*		*Difference*	
	Carbon (per cent) I	*Hydrogen (per cent) II*	*Carbon (per cent) III*	*Hydrogen (per cent) IV*	*Carbon I − III*	*Hydrogen II − IV*
10713	77·28	5·08	76·88	5·10	0·40	−0·02
10936	82·84	4·40	82·51	4·42	0·33	−0·02
24325	76·07	5·52	76·10	5·49	−0·03	0·03
24326	69·26	5·02	69·40	5·00	−0·14	0·02
24327	67·18	5·06	67·16	5·01	0·02	0·05
24328	77·59	5·49	77·52	5·53	0·07	−0·04
24219	82·19	5·04	82·02	5·09	0·17	−0·05
24226	81·68	5·04	81·58	5·04	0·10	*Nil*
24293	79·80	5·16	79·56	5·15	0·24	0·01
24296	77·25	4·72	77·06	4·74	0·19	−0·02
24432	76·10	4·62	75·70	4·68	0·40	−0·06
24436	77·62	4·70	77·54	4·72	0·08	−0·02
24440	75·56	4·56	75·28	4·65	0·28	−0·09
24731	74·62	5·09	74·44	5·13	0·18	−0·04
24704	76·84	4·62	76·65	4·72	0·19	−0·10
24723	78·70	5·21	78·32	5·30	0·38	−0·09
23422	73·03	4·82	72·99	4·84	0·04	−0·02
23429	81·36	5·13	81·56	5·19	−0·20	−0·06
24744	77·38	5·06	77·11	5·06	0·27	*Nil*
24749	81·37	5·24	81·08	5·21	0·29	0·03
24657	78·94	4·94	78·84	4·88	0·10	0·06
24669	83·02	4·94	83·08	5·00	−0·06	−0·06
25000	81·84	4·94	81·62	5·03	0·22	−0·09
25057	74·63	4·94	74·58	4·94	0·05	*Nil*
24696	85·56	5·02	85·14	4·99	0·42	0·03
25063	75·08	5·00	74·80	5·01	0·28	−0·01
25075	72·68	5·02	72·41	5·00	0·27	0·02
23876	74·51	5·08	74·20	5·12	0·31	−0·04
23881	73·48	4·91	73·30	4·92	0·18	−0·01

Belcher and Ingram tube were treated separately from those obtained with a U-tube filled with manganese dioxide. In both cases the difference between the carbon values for the two methods (with and without manganese dioxide tubes) was significant at the 1 in 1 000 level. It is clear, therefore, that the carbon values obtained by the Liebig method will be erroneously high unless an absorber for oxides of nitrogen is included in the absorption train.

The algebraic average differences for carbon and hydrogen for the 29 coals examined are:

Carbon (per cent)	Hydrogen (per cent)
0·17	− 0·02

The difference observed for the hydrogen value was not considered to be significant.

OXIDES OF NITROGEN IN THE SHEFFIELD HIGH TEMPERATURE METHOD

Normal combustions were carried out on two coals in duplicate by the High Temperature method but as for the estimation of oxides of nitrogen and sulphur in the Liebig method, the absorption train was replaced by a sintered glass bubbler containing a 1 per cent solution of hydrogen peroxide in 0·1N sulphuric acid and nitrate subsequently determined with phenol–disulphonic acid. The results are reported in *Table 4* with and without the use of a silver roll employed for the retention of oxides of sulphur. They indicate that oxides of nitrogen are also formed in the High Temperature method but that the amounts are negligible and there is no necessity for the use of manganese dioxide absorbers in the High Temperature method though one may be placed in the absorption train for the absorption of acidic oxides purely as a precautionary measure.

Table 4. Oxides of nitrogen in the High Temperature method

Experiment	*As* NO_2 (*Coal basis: per cent*)	
	Coal 16650	*Coal 16642*
With silver roll	0·15	0·19
Without silver roll	0·15	0·21

CONCLUSIONS

(*1*) Oxides of nitrogen equivalent to approximately 0·2 per cent of carbon are evolved during a Liebig determination of carbon and hydrogen on coal; the amounts evolved in the High Temperature method are negligible.

(*2*) Complete retention of oxides of sulphur is obtained in a properly packed Liebig tube.

(*3*) Nitrogen dioxide is satisfactorily removed by a Belcher and Ingram manganese dioxide tube, though an ordinary U-tube, which has the advantage of containing more reagent, works equally well and may have a longer life.

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The Rapid Analysis of Coal Ash, Slag and Boiler Deposits

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A detailed description is given of the methods now used by the B.C.U.R.A. for the rapid, complete analysis of inorganic residues from coal; these methods are of general applicability to the analysis of coal ash, clinker, slag, boiler dusts and deposits. The precise instructions for determining the individual constituents are based on an extensive investigation, involving more than 1 000 analytical determinations, in which the results given by the rapid and by classical procedures were compared. Notes on this experimental work, together with the comparative analyses, are given in the Appendix.

Two solutions are prepared for analysis, one from a fusion of the sample with sodium hydroxide for the determination of silicon and aluminium, the other from a digestion of the sample with hydrofluoric and sulphuric acids for the determination of all other commonly occurring constituents except sulphur. Colorimetric procedures are used for silicon (silico-molybdenum blue), aluminium (calcium alizarin red-S complex), iron and titanium (tiron), manganese (permanganate), and phosphorus (phospho-vanado-molybdate). A 'Unicam S.P.600' spectrophotometer is used for the measurement of the optical densities of all the coloured solutions. Calcium and magnesium are determined by titration with the disodium salt of ethylene diamine tetra-acetic acid (EDTA) using calcein (for calcium) and screened o-cresol-phthalein complexone (for calcium plus magnesium) as indicators. An 'Eel' flame photometer is used for the determination of sodium and potassium. Sulphur is determined gravimetrically on a separate sample.

The methods are particularly suitable for batch analysis and five samples can be analysed in duplicate in a week by one analyst with an accuracy that is better than 0·4 per cent for all constituents except Al_2O_3, *for which the accuracy is, at present, about 1·0 per cent.*

ONE of the important factors common to all industrial usage of coal—combustion, gasification and carbonization—is the fate of the associated inorganic minerals. While, in any particular instance, the type of residue produced is determined by plant conditions, its quantity and, most probably, its troublesome nature, are dictated by the minerals originally present in the coal. These inorganic residues include clinkered ash, slag, loose and bonded boiler deposits, and fine particulate ash which could, for example, lead to problems of atmospheric pollution.

During the researches by the B.C.U.R.A. all these materials are produced and, although it is a knowledge of some physical property which may be required, a chemical analysis is frequently the quickest or best method of characterization. For example, the flow properties of a slag are at present more readily obtainable from chemical analysis on the basis of known correlations with the 'silica ratio'[1] than by the determination of the viscosity of the slag. Similarly, the nature of deposits on boiler heat-exchange surfaces may be classified according to their chemical analysis. The type of analysis needed and the accuracy required have to be considered in relation to each research project and may vary from a complete analysis in duplicate with the best possible accuracy to, say, a simple test of the water-soluble content of

the sample. However, the main demand is for the quick delivery of results which are comprehensive and reasonably accurate.

Following the modern trend, physicochemical methods have been examined with particular emphasis on their application to the wide range of concentrations of the elements which are found in the different varieties of coal residue. Similarly, the effect of some interfering ions on specific determinations has required study. As a result of these investigations, the proposed methods are generally applicable to this class of material. The investigational work is covered in the Appendix and is supported by an extensive series of comparisons with results from classical procedures. Of course, it has not been practicable to cater for every eventuality and it is possible that a combination of extreme concentrations outside those studied, or the presence of abnormal constituents, could lead to inaccuracies.

BRIEF REVIEW OF POSSIBLE METHODS

Classical analytical procedures for coal ash analysis are given in *B.S. 1016: 1942*[2], and in Fuel Research Board *Survey Paper No. 50*[3]. While it may be claimed that these are the most accurate methods, they are unfortunately very time-consuming and laborious—chiefly because chemical separations are the basis of much of the analysis. This also is true, but to a more limited extent, of the methods of H. E. CROSSLEY and A. H. EDWARDS[4], A. H. EDWARDS[5], and A. H. EDWARDS and D. FLINT[6] for the analysis of boiler deposits.

In recent years, the introduction of physicochemical techniques for making the final measurements in analysis with consequent elimination of lengthy chemical separations, has led to a considerable speeding up of analysis with, usually, some slight loss of accuracy. Spectrographic[7], chromatographic[8] and polarographic[9] methods have all been applied recently to the analysis of one or more constituents of coal ash. R. HEDIN[10] has proposed a rapid colorimetric method for the analysis of silicate materials. His work has been reviewed by several authors[11,12] and the results obtained agreed well with the 'classical' analyses. A rapid method specifically for coal and oil ash, including procedures for vanadium and germanium, was developed by B. A. COLLISS and N. N. BANNERJEE[13]. Other workers developed methods involving rapid precipitation and colorimetric techniques[14,15]. R. COREY and M. JACKSON[16] have also presented a scheme for the rapid semimicro analysis of silicates which involves colorimetric and flame photometric techniques. The method is rapid, but wet chemical separations are still included for the gravimetric determination of silicon and for the separation of iron, titanium and aluminium from calcium and magnesium.

Methods applicable to silicate rocks have been devised by L. SHAPIRO and W. W. BRANNOCK[17,18] The accuracy of their earlier scheme (1952) has recently been examined by E. L. P. MERCY[19]. A convincing feature of their recent work (1956) is the large number of results for standard mixtures that they quote; and the methods developed by the B.C.U.R.A. for the analysis of inorganic coal residues follow the pattern but not the detail of their general scheme.

METHODS OF ANALYSIS

Sample preparation

About 3 g of material, ground to pass a 200 mesh B.S. test sieve, is sufficient for duplicate analysis. However, the method of preparation of the various samples of ash, slag and deposit for analysis cannot be generalized owing to the different character of the materials to be examined. A few notes for guidance are given here of some of the difficulties that may be encountered.

Ash from coal samples—This should be prepared according to the British Standard method[20]. The heating conditions and the depth of the coal layer in the dishes should be rigidly followed so that, for a given sample, a constant amount of sulphate is retained in the ash.

Moisture and carbon dioxide are readily absorbed by the ash during its size reduction, and on storing. The sample should therefore be ignited at 800°C to constant weight (usually 1 hour will suffice) before it is used for analysis.

Slags—Most slags are extremely hard, and a major difficulty in the preparation of the analysis sample is the avoidance of contamination by material removed from the crushing and grinding surfaces. Over-grinding in the early stages of preparation must be avoided, and it is preferable to use an agate pestle and mortar for the final stages.

There may be free iron in a slag sample, either because it was present in the bulk sample or else picked up by contamination. It can be removed prior to the final stages of preparation and, if necessary and applicable, a correction can be made to the analytical results.

Boiler deposits (including flue dusts, clinker, etc.)—A full description of the general nature of these deposits is given in the *Technical Paper No. 2* issued by the Boiler Availability Committee[21]. These samples are often wet and acidic, and it is advisable to determine the loss on drying at 110°C of a portion of the sample (up to 3 g) before grinding. A careful examination of the sample before the grinding process is suggested and, if necessary, discrete particles of boiler tube scale, refractory brick, etc., should be separated.

General scheme of analysis

The scheme of analysis recommended by Shapiro and Brannock[18] has been broadly followed, but modifications have been necessary in order to obtain a general-purpose method satisfactory for the analysis of inorganic coal residues using existing (and relatively common) equipment; different methods have been included for iron, calcium, magnesium, sodium and potassium, and modifications made in those for silicon and aluminium. The proposed scheme is given in *Figure 1.*

The determinations of silicon and aluminium in aliquot parts of solution A are made by measuring the optical density with a 'Unicam S.P.600' spectrophotometer. Operation of this instrument has been adequately described elsewhere[22]. It is, however, important to use two matched cells always placed in the same position for all optical density measurements. To obtain the desired level of accuracy for silicon and aluminium—usually major constituents—it is necessary to include duplicates of a reference standard (N.B.S. Sample

No. 99, feldspar[23]—see Appendix, *Table 1*) with each batch of samples, rather than rely on the use of chemical standards. A blank determination is also made.

There are three quite different techniques used for completing the determinations on the aliquot parts of solution B. Iron, manganese, titanium and phosphorus are determined on the spectrophotometer although, for these

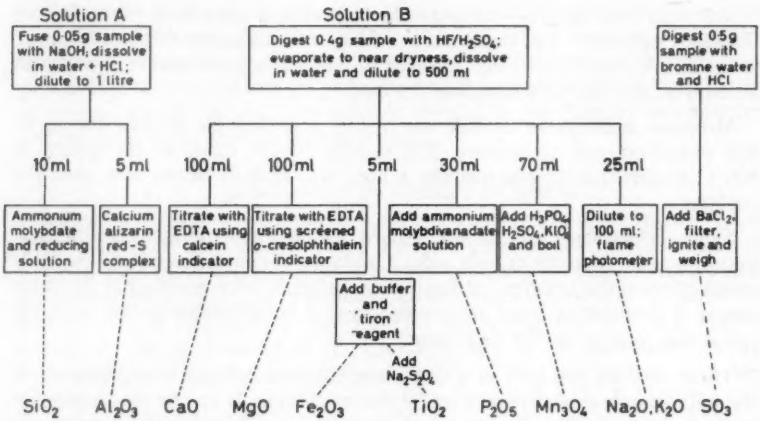

Figure 1. Proposed scheme for rapid analysis of coal ash, slag and boiler deposits

constituents, reference standards are prepared directly from the appropriate chemical reagents of analytical quality. Calcium and magnesium are determined by titration with the disodium salt of ethylene diamine tetra-acetic acid (EDTA); and sodium and potassium are determined on the 'Eel' flame photometer. The use of this instrument has also been described elsewhere[24]. Two blank solutions are prepared with each batch of samples for solution B treatment. The use of the duplicate blank solutions leads to a rather better accuracy for sodium and potassium although only one is necessary for the determination of the remaining constituents.

The aliquot parts specified for the determinations to be made on solution B are suitable for the range of concentrations of constituents likely to be found in typical British coal ashes. However, it may occasionally be necessary to reduce an aliquot. This should be done by taking a suitable smaller volume and making it up to the specified aliquot volume by dilution with some of the blank solution.

The sulphur content of a batch of samples is determined gravimetrically. An additional test is made on a solution of known sulphur content in order to obtain the reagent blank.

Instructions under the 'Procedure' for each of the determinations are numbered so as to break the sequence of operations at suitable points to permit the correct handling of batch analysis and, unless otherwise stated,

each numbered step should be completed for all the solutions in the batch before proceeding to the next step.

Preparation of analysis solutions

Special reagents—

Sodium hydroxide	Crush 1·5 g of pellets immediately before addition to each crucible
Hydrofluoric acid	40 per cent (w/w)
Sulphuric acid	Dilute 50 per cent (v/v)
Hydrochloric acid	Dilute 50 per cent (v/v).
Reference standard	N.B.S. Sample No. 99 (Soda feldspar)

Solution A

(*1*) Weigh accurately (on a semimicro balance, if available) about 0·05 g of each sample and two 0·035 g portions of the reference standard. Transfer each to a 40 ml nickel crucible. Another crucible is required for a blank solution.

(*2*) Add 1·5 g of freshly powdered sodium hydroxide to each crucible. Cover and heat the contents over a micro bunsen burner for 5 minutes at dull red heat taking care to ensure that the sample is not floating upon the molten sodium hydroxide. Allow to cool.

(*3*) Half fill the crucibles with water, cover and allow to stand at least 1 hour. (Overnight if convenient.)

(*4*) By means of a long-stem plastic funnel, transfer the contents of each crucible into a separate 1 litre graduated flask containing about 400 ml of water and 20 ml of the hydrochloric acid. With the aid of a rubber 'policeman' remove and wash any residue into the appropriate flask. Dilute to the mark with water and mix well. (Any slight turbidity disappears on standing.)

Solution B

(*1*) Weigh accurately about 0·4 g of each sample into a 35 ml platinum crucible. Two further crucibles are required for blank solutions.

(*2*) Add 1·5 ml of the sulphuric acid.

(*3*) Add about 10 ml of the hydrofluoric acid.

(*4*) Place the lids on the crucibles and digest (overnight) on a water bath.

(*5*) Remove and rinse the covers and allow the solutions to evaporate on the water bath until most of the hydrofluoric acid and free water are removed.

(*6*) Transfer on to a hot-air bath and evaporate to strong fumes of sulphuric acid, for 10 minutes.

(*7*) Cool, add 1 ml of the sulphuric acid and 1 ml concentrated nitric acid and evaporate to fumes of sulphuric acid for a further 10 minutes.

(*8*) Cool, and nearly fill the crucible with water.

(*9*) Digest on a water bath for half an hour. Cool and transfer to 500 ml graduated flasks. Dilute to the mark and mix. Some calcium sulphate may remain after digestion. This slowly dissolves on dilution in the 500 ml flask. With some samples a small residue (possibly barium sulphate, corundum, etc.) may still remain, but for most purposes may be neglected.

Determination of silicon

The method described by W. E. BUNTING[25] is employed. The yellow silicomolybdate complex is reduced to molybdenum blue and the optical density of the solution is measured at 650 mμ.

Special reagents—

Ammonium molybdate solution	Dissolve 7·5 g of ammonium molybdate in 75 ml of water. Add 10 ml of 50 per cent (v/v) sulphuric acid and dilute to 100 ml. Store in a plastic bottle
Tartaric acid solution	10 per cent (w/v). Store in a plastic bottle
Reducing solution	Dissolve 0·7 g sodium sulphite in 10 ml of water. Add 0·15 g of 1-amino-2-naphthol-4-sulphonic acid and stir until dissolved. Dissolve 9 g of sodium metabisulphite in 90 ml of water and add this solution to the solution above and mix. Store in a plastic bottle.

Procedure—

(*1*) Pipette into separate 100 ml graduated flasks 10 ml of each sample solution A, 10 ml of each reference standard solution, and 10 ml of the blank solution. Dilute to 50 to 60 ml with water and mix.

(*1*) Add 1 ml of the ammonium molybdate reagent from a pipette, swirling the flasks during the additions. Mix well and allow to stand for 10 minutes.

(*3*) Pipette 4 ml of the tartaric acid solution followed immediately by 1 ml of the reducing solution into one flask, swirling the flask during the additions, dilute immediately to volume and mix. This step must be completed before passing on to the next flask.

(*4*) After a minimum time of 1 hour determine the optical density of the sample, the blank and of the reference standard solutions (all compared with water) at 650 mμ with the spectrophotometer, using 2 cm cells. The colour is stable.

Calculations—

Calculate the optical density readings to a 50 mg basis thus

$$\frac{\text{optical density (corrected for blank)} \times 50}{\text{wt of sample in mg}}$$

Let D_1 = optical density reading of sample on 50 mg basis
D_2 and D_3 = optical density readings of reference standards on 50 mg basis
S = percentage of silica (SiO_2) in reference standard.
Then percentage of silica in sample

$$= D_1 \times S \times 2/(D_2 + D_3)$$

Determination of aluminium

Aluminium is determined by measuring the optical density at 475 mμ of a solution containing the complex of aluminium, calcium and alizarin red-S[26]. The effect of iron is minimized by the formation of a complex with thioglycollic acid prior to adding the alizarin red-S.

Special reagents—

Hydroxylamine hydrochloride solution	10 per cent (w/v)
Calcium chloride	Dissolve 14 g calcium carbonate in 50 ml of 50 per cent (v/v) hydrochloric acid and boil the solution for 2 minutes. Cool and dilute to 1 litre
Thioglycollic acid	5 per cent (v/v)
Buffer solution	Dissolve 140 g of sodium acetate in water, add 60 ml of glacial acetic acid and dilute to 1 litre
Alizarin red-S solution	0·1 per cent (w/v).

Procedure—

(*1*) Pipette into separate 100 ml graduated flasks 5 ml of each sample solution A, 5 ml of each reference standard solution, and 5 ml of the blank solution.

(*2*) Add 2 ml of the calcium chloride solution to each flask and mix.

(*3*) Add 1 ml of the hydroxylamine hydrochloride solution to each flask and mix.

(*4*) Add 1 ml of the thioglycollic acid to each flask and mix.

(*5*) Add 10 ml of the buffer solution to each flask and mix.

(*6*) Add 5 ml of the alizarin red-S solution to each flask, dilute to 100 ml with water, mix, and allow to stand for 3 hours.

(*7*) Check for cell differences by placing the blank solution in each cell, and measuring the difference in optical density at 475 mμ with the spectrophotometer, using 2 cm cells.

(*8*) Determine the optical density of the sample and the reference standard solutions (compared with the blank).

Calculations—

Calculate the optical density readings to a 50 mg basis thus

$$\frac{\text{optical density} \times 50}{\text{wt of sample in mg}}$$

Let D_1 = optical density reading of sample on 50 mg basis
D_2 and D_3 = optical density readings of reference standards on 50 mg basis
S = percentage of aluminium oxide (Al_2O_3) in reference standard.
Then percentage of aluminium oxide in sample

$$= D_1 \times S \times 2/(D_2 + D_3)$$

Determination of iron and titanium

Iron is determined by measuring the optical density at 560 mμ of a solution containing the violet complex of ferric iron with 'tiron' (disodium-1,2-dihydroxybenzene-3,5-disulphonate)[27]. The pH of the solution for colour development is buffered to about 4·9, this being also satisfactory for the subsequent titanium determination[28].

The violet-coloured solution is treated with sodium dithionite to reduce the iron complex, and the yellow colour produced by the reaction of titanium with 'tiron' is measured at 430 mμ.

Special reagents—

'Tiron' solution	Dissolve 3·25 g 'tiron' in water and dilute to 50 ml. Prepare immediately before use
Buffer solution	Dissolve 40 g ammonium acetate in water, add 15 ml glacial acetic acid and dilute to 1 litre
Sodium dithionite	Dry powder ($Na_2S_2O_4$)
Standard iron solution	Weigh 0·5893 g of ferrous ammonium sulphate into a 400 ml beaker, add 100 ml of water, 6 ml of 50 per cent (v/v) sulphuric acid and a few drops of 100 vol. hydrogen peroxide. Boil to remove excess hydrogen peroxide. Cool and dilute to 1 litre in a graduated flask (5 ml ≡ 0·6 mg Fe_2O_3)
Standard titanium solution	Weigh 4·500 g titanyl potassium oxalate and 8·0 g ammonium sulphate into a Kjeldahl flask. Add 50 ml concentrated sulphuric acid and heat gradually. Boil for 10 minutes. Cool and dilute to 1 litre. Dilute 10 ml of this solution to 1 litre with 2·5 per cent (v/v) sulphuric acid (5 ml ≡ 0·05 mg TiO_2).

Procedure—

(*1*) Pipette into separate, dry 100 ml beakers, 5 ml of each sample solution B, 5 ml of the blank solution, two 5 ml portions of the standard iron solution and two 5 ml portions of the standard titanium solution.

(*2*) Pipette 2 ml of the 'tiron' solution into each beaker.

(*3*) With a pipette add 50 ml of the buffer solution. Mix thoroughly.

(*4*) *To determine iron*, measure the optical density of a portion of each of the sample solutions, the standard iron solutions, and the blank solution (all compared with water) at 560 mμ with the spectrophotometer, using 1 cm cells. The density may be measured immediately and the colour is stable for at least 2 hours.

(*5*) *To determine titanium*, add about 10 to 20 mg of the sodium dithionite powder to each of the remaining solutions in the beakers, and mix by gently rotating. Allow to stand for about 1 minute, and measure the optical density of the titanium complex at 430 mμ, using 4 cm cells.

Calculations—

$$\text{Percentage of iron oxide } (Fe_2O_3) = \frac{6 \times \text{optical density of sample (corrected for blank)}}{\text{mean optical density of Fe standards} \times \text{wt of sample in g}}$$

$$\text{Percentage of titanium dioxide } (TiO_2) = \frac{0{\cdot}5 \times \text{optical density of sample (corrected for blank)}}{\text{mean optical density of Ti standards} \times \text{wt of sample in g}}$$

Determination of manganese

Manganese is determined by measuring the optical density at 525 mμ of a solution in which the manganese has been oxidized to permanganate with potassium periodate.

Special reagents—

Potassium periodate	Crystals
Phosphoric acid	Sp.gr. 1·75
Standard manganese solution	Dissolve 1·036 g potassium permanganate in about 500 ml water. Reduce the solution with sulphur dioxide, boil off the excess gas, and dilute to 1 litre with water. Dilute 10 ml of this solution to 1 litre to prepare working standard (70 ml ≡ 0·35 mg Mn_3O_4).

Procedure—

(*1*) Pipette into separate 250 ml beakers, 70 ml of each sample solution B, 70 ml of blank solution B and two 70 ml portions of standard manganese solution.

(*2*) Add to each beaker 3 ml of concentrated sulphuric acid, 1 ml of the phosphoric acid and 0·5 g of the potassium periodate.

(*3*) Cover the beakers and boil the contents for 5 minutes. Keep hot for half an hour.

(*4*) Allow to cool and transfer to 100 ml graduated flasks, dilute and mix.

(*5*) Determine the optical density at 525 mμ of the samples, the standard manganese solutions, and the blank solution (all compared with water), using 4 cm cells.

Calculation—

$$\text{Percentage of manganese oxide } (Mn_3O_4) = \frac{0{\cdot}25 \times \text{optical density of sample (corrected for blank)}}{\text{mean optical density of standards} \times \text{wt of sample in g}}$$

Determination of phosphorus

Phosphorus is determined by measuring the optical density at 430 mμ of a solution containing the yellow ammonium phospho-vanado-molybdate complex[29].

Special reagents—

Molybdivanadate solution	Dissolve 1·25 g of ammonium metavanadate in 400 ml of 50 per cent (v/v) nitric acid. Dissolve 50 g of ammonium molybdate in 400 ml water. Pour the ammonium molybdate solution into the ammonium vanadate solution, dilute to 1 litre and mix
Standard phosphorus solution	Dissolve 0·4001 g of anhydrous sodium orthophosphate (Na_2HPO_4) (dried at 120°C) in water and dilute to 1 litre. Dilute 50 ml of this solution to 1 litre (30 ml ≡ 0·30 mg P_2O_5).

Procedure—

(*1*) Pipette into separate 50 ml graduated flasks, 30 ml of each sample solution B, 30 ml of blank solution B and two 30 ml portions of standard phosphorus solution.

(*2*) Pipette 10 ml of molybdivanadate solution into each flask, swirling the flask during the addition. Dilute to 50 ml, mix, and allow to stand for at least 5 minutes.

(*3*) Determine the optical density at 430 mμ of the samples, the standard phosphorus solutions, and the blank solution (all compared with water), using 4 cm cells.

Calculation—

$$\text{Percentage of phosphorus pentoxide } (P_2O_5) = \frac{0{\cdot}5 \times \text{optical density of sample (corrected for blank)}}{\text{mean optical density of standards (corrected for blank)} \times \text{wt of sample in g}}$$

Determination of calcium and magnesium

Calcium and magnesium are determined by titration with EDTA in a manner similar to that of Bennett *et al.*[14]. No ammonia precipitation is carried out, the iron, aluminium and titanium being complexed with triethanolamine. Screened indicators, also favoured by other authors[30, 31], are used.

Special reagents—

Triethanolamine solution	Dilute 500 ml triethanolamine to 1 litre with distilled water and mix thoroughly
Sodium hydroxide solution	Dissolve 160 g sodium hydroxide in water and dilute to 1 litre. Store in a plastic bottle
Standard calcium solution	Dissolve 1·785 g of calcium carbonate, dried at 110°C, in 100 ml of 4 per cent (v/v) hydrochloric acid. Boil to expel carbon dioxide, cool and dilute to 1 litre (1 ml ≡ 1 mg CaO)
EDTA solution	Dissolve 6·6 g of the disodium salt of ethylene diamine tetra-acetic acid in water and dilute to 1 litre. Standardize against the standard calcium solution, using calcein or *o*-cresolphthalein complexone as indicator
Calcein indicator	Mix thoroughly 0·2 g calcein, 0·12 g thymolphthalein and 20 g finely ground potassium chloride
o-Cresolphthalein indicator	Dissolve 0·1 g *o*-cresolphthalein complexone, 0·005 g methyl red, and 0·05 g paramine green BN in a few drops of ammonia solution and dilute to 100 ml. This solution should be freshly prepared each week.

Procedure for calcium—

(*1*) Pipette into separate 500 ml conical flasks 100 ml of each sample solution B and 100 ml of the blank solution.

(*2*) Add 20 drops of concentrated hydrochloric acid, 5 ml of the triethanolamine solution, 5 ml of ammonia solution (0·880 sp. gr.), and 10 ml of the sodium hydroxide to each flask, mixing thoroughly after the addition of each reagent.

(*3*) Dilute to about 200 ml with water.

(*4*) Add about 40 mg of calcein indicator to one flask and titrate against the standardized EDTA solution until the colour changes from a green fluorescence to purple. The end point is reached when the purple colour is not intensified by the addition of more EDTA solution.

Procedure for magnesium—

(*1*) Pipette into separate 500 ml conical flasks 100 ml of each sample solution B and 100 ml of the blank solution.

(*2*) Add 20 drops of concentrated hydrochloric acid, 20 ml of the triethanolamine solution, and 25 ml of ammonia solution (0·880 sp. gr.) to each flask, mixing thoroughly after the addition of each reagent.

(*3*) Dilute to about 200 ml with water.

(*4*) Add a volume of EDTA slightly less than the calcium titre, add 0·5 ml of the *o*-cresolphthalein indicator, and continue the titration until the colour changes from pale purple to colourless or very pale grey. An excess of about 0·2 ml of EDTA produces a green coloration.

Calculations—

Let v_1 = volume of EDTA required for calcium titration, corrected for blank.

v_2 = volume of EDTA required for calcium plus magnesium titration, corrected for blank.

F = No. of mg CaO ≡ 1 ml EDTA.

W = weight of sample in grammes.

Then percentage of calcium oxide (CaO) $= v_1 \times F/2W$

and percentage of magnesium oxide (MgO) $= (v_2 - v_1) \times 0{\cdot}3595 \times F/W$

Determination of sodium and potassium

An 'Eel' flame photometer is used for the determination of the alkali oxides. In order to minimize possible contamination from glass vessels, these determinations should follow on immediately after the preparation of solution B. Investigation has shown that correction for calcium interference is normally unnecessary.

Special reagents—

Standard sodium plus potassium solution — Dissolve 0·1886 g sodium chloride and 0·1583 g of potassium chloride (both dried at 400°C) in distilled water and dilute to 1 litre. This solution contains 100 p.p.m. Na_2O + 100 p.p.m. K_2O. Dilute 10 times to prepare the working standard, 10 p.p.m. Na_2O + 10 p.p.m. K_2O. Store in plastic bottles.

Procedure—

(*1*) Pipette into separate 100 ml graduated flasks 25 ml of each sample solution B and 25 ml of each of the two blank solutions. (If a sample is known to contain more than 5 per cent of either sodium oxide or potassium oxide reduce the aliquot.) Dilute to the mark and mix.

(*2*) Set the zero of the galvanometer on the flame photometer using distilled water with the sodium filter in position.

(*3*) Set the full scale galvanometer reading with the standard solution containing 10 p.p.m. Na_2O + 10 p.p.m. K_2O.

(*4*) Record the galvanometer deflection of the solutions.

(*5*) Repeat steps 2, 3 and 4 with the potassium filter in position.

(*6*) Calculate the percentages of oxides of sodium and potassium by using calibration curves and making appropriate corrections for the mean of the blank solutions.

Preparation of calibration curves—Add from a burette aliquot parts of 5, 10, 15, 20, 25, 30, 35, 40 and 45 ml of the 100 p.p.m. Na_2O + 100 p.p.m. K_2O solution into separate 500 ml graduated flasks and dilute with water to the mark. Then proceed as in steps 2, 3, 4 and 5 above. Prepare calibration curves of the galvanometer readings plotted against Na_2O and K_2O concentrations. These curves should be checked on their initial preparation and rechecked at intervals of about six months.

Determination of sulphur

The sample is extracted with bromine water and hydrochloric acid, and the sulphate determined gravimetrically as barium sulphate.

Special reagents—

Bromine water	Saturated
Hydrochloric acid	10 per cent (v/v)
Barium chloride solution	Dissolve 100 g of barium chloride ($BaCl_2.2H_2O$) in distilled water and dilute to 1 litre
Potassium sulphate solution	Dissolve 2·1741 g of potassium sulphate, (previously dried at 110°C for 2 hours) in distilled water and dilute to 1 litre 25·00 ml ≡ 0·0100 g sulphur ≡ 0·0728 g $BaSO_4$.
Methyl red indicator	

Procedure—

(*1*) Weigh accurately about 0·5 g of each sample and transfer into separate 250 ml beakers. Two further beakers are required for the blanks.

(*2*) Add 5 ml of the bromine water to the beakers. If the bromine is decolorized add a further 5 ml of bromine water.

(*3*) Add 100 ml of the hydrochloric acid, cover the beakers and boil for 1 hour.

(*4*) Filter through a close-textured paper or pad into 400 ml beakers, washing the paper or pad with four 20 ml portions of hot distilled water.

(*5*) Neutralize the filtrates with ammonia solution (0·880 sp. gr.) using the methyl red as indicator, and add 1 ml of concentrated hydrochloric acid.

(*6*) Dilute each solution to about 200 ml with water and add 25·00 ml of the potassium sulphate solution to the blank solutions (and to any samples suspected of having a very low sulphur content).

(*7*) Heat the covered beakers until the solutions boil, add 10 ml of the cold barium chloride solution from a pipette held so that the liquid falls into the middle of the hot solution, and maintain just below the boiling point for 30 minutes.

(*8*) Filter, wash, ignite and weigh.

Calculation—

Let W_1 = weight of sample taken (g)

W_2 = weight of barium sulphate found (g)

W_3 = weight of barium sulphate found in blank (g)

Then percentage sulphur (as SO_3) = $\{W_2 - (W_3 - 0{\cdot}0728) \times 34{\cdot}3\}/W_1$

DISCUSSION

The development of faster and more accurate methods is a continuous process in most analytical laboratories, and the methods described here are a part of this process. In this instance, the objective has been to speed up the analysis of such materials as slags, ashes and deposits by means of a universal method that entails only a minimum loss of accuracy. Samples are still received, however, where maximum accuracy is required and where classical procedures must be carried out. This is time-consuming, but it does provide a series of samples of known content which can be used for investigational work on new or modified methods.

To a limited extent, the direction of the investigations leading up to the proposed methods are determined by existing equipment. Thus, while the flame photometer was introduced at an early stage specifically for the determination of sodium and potassium, the determinations of other constituents have been developed around an existing spectrophotometer.

The notes which follow, in the Appendix, give details of the investigation of some of the rapid methods together with evidence on their repeatability and accuracy. Only those methods which needed fairly extensive checking are covered, the remaining methods—for titanium, manganese, phosphorus and sulphur—being accepted as well-established and accurate procedures. Studies have been made of limits of concentration, pH, wavelength, interfering elements, etc.

The *Tables 3* to *8* in the Appendix give a series of comparative values for the rapid and the classical procedures for specific constituents on a variety of samples. It was not possible to use the same samples throughout the work as the methods were investigated one after the other over a period of time, and some of the earlier samples were used up. The duplicates quoted for the rapid methods were in all cases determined on separately weighed fractions of the samples and not simply from 'another aliquot'. Although only one value is given for the classical results it is, in fact, a mean of two with a normal repeatability of $\pm$ 0·1 per cent absolute for all constituents. The measure of agreement with the classical results can be used as a criterion of the accuracy

of the rapid methods. Values for this accuracy, together with values for the repeatability are summarized for all constituents in *Table 9*.

A further indication of the accuracy of any scheme for 'complete' analysis lies in the proximity to 100 of the sum of the percentages of constituents in any given sample. *Table 10* shows complete analyses of a coal ash, a slag and a boiler residue carried out by both the classical and the rapid methods. A large number of samples has been analysed by the rapid methods and, in general, the sum of the constituents has been within 99 to 101 per cent. Any values that occur much outside this range indicate the need for further examination of the sample.

The time-saving with the rapid methods is considerable, a complete analysis taking less than one fifth of the time required for a classical analysis. With the detailed, stepwise procedures given, a batch of ten samples (or five in duplicate) can be handled comfortably, and their complete analyses for eleven constituents requires about a week.

The work described here forms part of a continuous programme on the speeding-up of methods of analysis of ashes, slags and deposits, with the minimum loss of accuracy. Further improvements to the proposed methods are being investigated with particular reference to the determination of aluminium and sulphur, and to the interference of abnormal concentrations of constituents such as phosphorus and iron. Also, modifications to the general scheme are being studied to accommodate constituents such as vanadium, copper and nickel that can be encountered in boiler deposits.

APPENDIX

NOTES ON THE DEVELOPMENT WORK AND COMPARATIVE RESULTS

(1) *Silicon*

Shapiro and Brannock's method[18] was first tried without modification but the results obtained were not in close agreement with those from classical procedures. The tendency was towards low results, of up to 1·5 per cent silica (absolute). The possibility of lack of decomposition of the sample was checked, but no trace of unattacked material was found after the sodium hydroxide fusion. (It should be noted that during this fusion, some light

Table 1. Analysis of N.B.S. Sample No. 99 (feldspar)

Constituent	%	*Constituent*	%
SiO_2	68·66	Na_2O	10·73
Al_2O_3	19·06	K_2O	0·41
Fe_2O_3	0·067	TiO_2	0·017
CaO	0·36	*Loss on ignition*	0·52
MgO	0·053		

samples of laboratory-prepared ash tended to float on the molten sodium hydroxide for more than 1 hour. Gentle swirling of the crucible was helpful in some cases, but was found to introduce the risk of loss of sample. The use of powdered flux placed on top of the sample was usually effective in preventing floating.)

Further investigation into the details of the method showed that (as recently reported by O. MENIS and D. L. MANNING[32]), the time interval between the addition of the tartaric acid and the reducing solution was critical. As shown in *Table 2*, the optical density of the silico-molybdenum complex decreases with increase of time interval between the addition of the

Table 2. Effect of time interval between adding tartaric acid and reducing solution

Time (min)	*Optical density (0·24 mg SiO_2/100 ml)*	*Time (min)*	*Optical density (0·24 mg SiO_2/100 ml)*
0	0·645	20	0·590
5	0·628	25	0·574
10	0·620	30	0·566
15	0·606		

Table 3. Comparison of methods for determining silicon

Sample No.	*Description of sample*	*% SiO_2 colorimetric*			*% SiO_2 classical*	*% SiO_2 (col.) − % SiO_2 (class.)*
				Mean		
S.2450	*Ash: Ellington H.M.*	20·1	20·0	20·0	20·2	−0·2
S.2545	*Ash: Cronton*	34·3	34·3	34·3	34·2	0·1
S.2551	*Boiler Deposit*	46·4	46·3	46·4	46·5	−0·1
S.2831	*Ash: Thoresby*	31·4	31·3	31·4	31·1	0·3
S.3034	*Ash: Thorne*	44·4	44·5	44·4	44·0	0·4
S.3035	*Ash: Thoresby*	46·7	46·8	46·8	46·7	0·1
S.3066	*Boiler Residue*	47·7	47·3	47·5	47·6	−0·1
S.3067	*Boiler Residue*	45·8	45·8	45·8	46·0	−0·2
S.3341	*Soot Ash*	37·7	37·8	37·7	38·0	−0·3
S.3343	*Ash: Wimblebury*	48·1	47·7	47·9	48·2	−0·3
S.3344	*Stack Dust*	47·4	47·9	47·7	47·5	0·2
S.3345	*Ash: Bentinck*	48·8	48·8	48·8	48·9	−0·1
S.3346	*Stack Dust*	45·7	46·1	45·9	46·1	−0·2
S.3360	*Ash: Barnsley Main*	54·3	54·4	54·3	54·4	−0·1
S.3368	*Slag: Bentinck*	49·7	49·7	49·7	49·3	0·4
S.3369	*Slag: Wimblebury*	50·3	50·6	50·4	50·3	0·1
S.3370	*Ash: Rasa (Yugoslavia)*	9·9	10·0	9·9	10·3	−0·4
S.3378	*Ash: Hamstead*	39·4	40·0	39·7	39·8	−0·1
S.3396	*Ash: Thoresby*	39·8	39·6	39·7	40·0	−0·3
S.3401	*Ash: Bentinck*	56·9	56·9	56·9	56·9	0·0
S.3402	*Slag: Hamstead*	41·2	41·6	41·4	41·5	−0·1
W–1	*Diabase*	52·3	52·6	52·5	52·6	−0·1
G–1	*Granite*	72·9	73·1	73·0	72·5	0·5

tartaric acid and reducing solution. This effect readily accounted for the variable results found in the earlier work when the tartaric acid was added to a batch of up to twelve sample solutions before any were reduced and diluted. In the proposed method the reducing solution is added immediately after the tartaric acid. Results using the proposed method are compared in *Table 3* with those from the classical analysis.

(2) *Aluminium*

Shapiro and Brannock[18] determined aluminium on an aliquot part of

solution A by measuring the optical density at 475 mμ of a solution containing the complex of aluminium, calcium and alizarin red-S. Iron and titanium also form complexes which absorb light at 475 mμ but the authors[18] claimed that any interference of iron was eliminated by the formation of ferrous ferricyanide in solution prior to the addition of alizarin red-S. A correction for the interference of titanium was applied by subtracting half the percentage of titanium dioxide from the apparent percentage of aluminium oxide (Al_2O_3).

Table 4. Comparison of methods for determining aluminium

Sample No.	*Description of sample*	% Al_2O_3 *colorimetric*			% Al_2O_3 *classical*	% Al_2O_3 (*col.*) − % Al_2O_3 (*class.*)
				Mean		
S.2434	*Coalite Slack*	22·6	22·6	22·6	23·0	−0·4
S.2450	*Ash: Ellington*	15·1	15·2	15·2	14·3	0·9
S.2545	*Ash: Cronton*	19·5	19·5	19·5	18·7	0·8
S.2551	*Boiler Deposit*	31·6	32·2	31·9	33·4	−1·5
S.2831	*Ash: Thoresby*	23·8	24·0	23·9	24·0	−0·1
S.3034	*Ash: Thorne*	22·2	23·2	22·7	22·6	0·1
S.3035	*Ash: Thoresby*	23·1	23·6	23·4	23·4	0·0
S.3066	*Boiler Residue*	19·9	21·0	20·5	20·6	−0·1
S.3067	*Boiler Residue*	19·8	20·1	19·9	19·7	0·2
S.3341	*Soot Ash*	23·9	24·4	24·2	25·3	−1·1
S.3343	*Ash: Wimblebury*	27·5	27·8	27·7	29·6	−1·9
S.3344	*Stack Dust*	28·5	28·8	28·6	29·5	−0·9
S.3345	*Ash: Bentinck*	22·7	22·9	22·8	23·2	−0·4
S.3346	*Stack Dust*	24·0	24·2	24·1	24·0	0·1
S.3368	*Slag: Bentinck*	24·5	24·8	24·6	24·7	−0·1
S.3369	*Slag: Wimblebury*	28·0	28·4	28·2	28·4	−0·2
S.3378	*Ash: Hamstead*	22·8	22·2	22·5	21·6	0·9
S.3396	*Ash: Thoresby*	21·8	21·7	21·7	20·8	0·9
S.3401	*Ash: Bentinck*	25·5	26·1	25·8	25·9	−0·1
S.3446	*Slag: Harraton*	28·1	27·9	28·0	28·2	−0·2
W–1	*Diabase*	15·7	15·9	15·8	15·2	0·6
G–1	*Granite*	14·4	14·7	14·6	14·3	0·3

When the method was examined a 10 ml aliquot was used, but for samples containing more than about 23 per cent of aluminium oxide (Al_2O_3), the colour developed deviated from Beer's law in the presence of other constituents of coal ash. A 5 ml aliquot was therefore used in all subsequent analyses. Investigations using standard aluminium solutions showed that iron still interfered to some extent, but that titanium at concentrations up to 2 per cent titanium dioxide showed no significant interference: these interferences become significant at abnormally low concentrations of aluminium.

The following general features were also checked. The wavelength used for measuring the optical density, the time of colour development, the pH of the solutions for colour development, and the time of standing between addition of the reagents. A slight improvement of the results was obtained by increasing the development time to 3 hours.

Other reagents that might form complexes with the iron were tried in place of the ferricyanide. The most successful was thioglycollic acid with which a colourless iron complex is formed in acid medium and with which the interference of iron was reduced.

Results using the proposed method are compared with classical analyses in *Table 4*. No correction is made for titanium or iron. Work is still in progress to improve the determination of this constituent.

(3) *Iron*

The choice of a colorimetric reagent for the determination of iron appears to be a matter of taste. Hedin[10] used thiocyanate; Shapiro and Brannock in their earlier work[17] developed the yellow ferric chloride colour; latterly[18], they used *o*-phenanthroline, which was also used by Pringle[15]. Thioglycollic acid was used by Bannerjee and Colliss[13] and by Mercy[19], whilst Corey and Jackson[16] used 'tiron'. A further reference in the literature[33] indicated that, although *o*-phenanthroline was the most specific for iron, by using 'tiron'[27], titanium could also be determined on the same solution with little extra effort. The latter method was therefore investigated.

Table 5. Comparison of methods for determining iron

Sample No.	*Description of sample*	% Fe_2O_3 *colorimetric*			% Fe_2O_3 *classical*	% Fe_2O_3 (*col.*) − % Fe_2O_3 (*class.*)
				Mean		
S.2434	*Ash: Coalite Slack*	23·28	23·48	23·4	23·1	0·3
S.2450	*Ash: Ellington H.M.*	37·19	37·19	37·2	37·7	−0·5
S.2869	*Ash: Cronton*	16·72	16·79	16·8	17·0	−0·2
S.2952	*Ash: Hapton Valley*	68·62	68·50	68·6	69·0	−0·4
S.3066	*Boiler Residue*	7·40	7·43	7·4	7·4	0·0
S.3067	*Boiler Residue*	8·02	7·83	7·9	8·1	−0·2
S.3204	*Ash: Thoresby*	12·57	12·48	12·5	12·7	−0·2
S.3296	*Ash: Cronton*	13·64	—	13·6	13·8	−0·2
S.3341	*Soot Ash*	12·37	11·73	12·1	12·1	0·0
S.3343	*Ash: Wimblebury*	5·83	5·83	5·8	5·8	0·0
S.3360	*Ash: Barnsley Main*	10·27	10·00	10·1	10·1	0·0
S.3368	*Slag: Bentinck*	8·33	8·59	8·5	8·2	0·3
S.3380	*Slag: Cronton*	16·49	16·35	16·4	16·1	0·3
S.3381	*Slag: Cronton*	11·55	11·41	11·5	11·1	0·4
S.3402	*Slag: Hamstead*	10·00	10·51	10·3	10·2	0·1
S.3413	*Slag: Bentinck*	7·80	7·59	7·7	7·6	0·1
S.3414	*Slag: Bentinck*	6·69	6·90	6·8	6·4	0·4
S.3415	*Slag: Bentinck*	5·95	5·96	6·0	6·0	0·0

The ferric iron complex with 'tiron' is sensitive to pH and to the quantity of 'tiron' reagent present. Although the red complex at pH 9·0 or the blue complex at pH 4·0 is normally used for the colorimetric determination of iron alone, in these studies the violet complex at pH 4·9 was used as this was known to be satisfactory for the subsequent determination of titanium. The violet complex adheres to Beer's law. Vanadium interferes with both the iron and titanium determinations but, as the amount of this element in ashes from British coals is small, except from a special type of vitrain occurring only in thin bands and fragments[34], its effect can be neglected.

The results of the 'tiron' method for iron are compared with classical analyses in *Table 5*.

(4) *Calcium and magnesium*

Considerable attention has been given to the application of ethylene diamine tetra-acetic acid (EDTA) for the analysis of calcium and magnesium in

Table 6. Comparison of methods for determining calcium and magnesium

Sample No.	Sample	Calcium oxide (as % CaO)				Magnesium oxide (as % MgO)			
		EDTA		Classical (oxalate)	EDTA − class.	EDTA		Classical ($Mg_2P_2O_7$)	EDTA − class.
			Mean				Mean		
S.2461	Ash: Ashton Moss Roger	6·69	6·7	6·7	Nil	3·38	3·4	3·9	−0·5
S.2545	Ash: Cronton	12·89, 12·72	12·8	13·1	−0·3	5·36, 5·56	5·5	5·6	−0·1
S.2961	Slag: Cronton	14·03, 14·06	14·0	14·0	Nil	5·84, 5·68	5·8	5·9	−0·1
S.3034	Ash: Thorne	7·31, 7·19	7·3	7·3	Nil	2·69, 3·02	2·9	3·2	−0·3
S.3066	Boiler Residue	11·16, 10·70 10·86, 10·90	10·9	11·1	−0·2	3·27, 3·34	3·3	3·6	−0·3
S.3067	Boiler Residue	11·98, 11·80	11·9	11·9	Nil	3·23, 3·36	3·3	3·7	−0·4
S.3189	Ash: Cronton	3·65, 3·93	3·8	3·8	Nil	2·46, 2·43	2·4	2·3	0·1
S.3191	Ash: Cronton	3·91, 3·94, 3·95	3·9	4·0	−0·1	2·55, 2·31, 2·33	2·4	2·5	−0·1
S.3204	Ash: Cronton	2·51, 2·57	2·5	2·5	Nil	1·73, 1·77	1·8	2·0	−0·2
S.3276	Ash: Bentinck	11·90, 11·78 11·45, 11·67	11·7	11·5	0·2	1·48, 1·62 1·62, 1·37	1·5	1·7	−0·2
S.3296	Ash: Cronton	3·92, 3·78 3·78, 3·90	3·8	3·8	Nil	1·89, 1·93 1·70, 1·67	1·8	2·0	−0·2
S.3327	Ash: Wimblebury	7·25, 7·13	7·2	7·2	Nil	1·40, 1·28	1·3	1·2	0·1
S.3341	Soot Ash	10·40, 10·43	10·4	10·4	Nil	2·20	2·2	2·3	−0·1
S.3343	Ash: Wimblebury	7·00, 7·04	7·0	6·7	0·3	1·35, 1·34	1·3	1·3	Nil
S.3345	Ash: Bentinck	10·45, 10·32	10·4	10·5	−0·1	1·46, 1·60	1·5	1·6	−0·1
S.3360	Ash: Barnsley Main	2·15, 2·20	2·2	2·4	−0·2	1·66, 1·75	1·7	1·8	−0·1
S.3368	Slag: Bentinck	10·62, 10·81	10·7	10·8	−0·1	1·34, 1·33	1·3	1·7	−0·4
S.3369	Slag: Wimblebury	7·45, 7·63, 7·65	7·6	7·6	Nil	1·29, 1·17, 1·18	1·2	1·3	−0·1
S.3370	Ash: Rasa (Yugoslavia)	32·11, 32·38	32·2	32·0	0·2	3·22, 3·33	3·3	2·9	0·4
S.3380	Slag: Cronton	4·18, 4·12	4·1	4·2	−0·1	2·10, 1·94	2·0	2·5	−0·5
S.3381	Slag: Cronton	2·71, 2·82	2·8	2·9	−0·1	1·98, 1·80	1·9	2·0	−0·1
S.3402	Slag: Hamstead	17·40, 17·36 17·56, 17·76	17·5	17·6	−0·1	1·04, 1·00 1·37, 1·05	1·1	1·5	−0·4
S.3413	Slag: Bentinck	5·37, 5·33	5·4	5·5	−0·1	1·15, 1·02	1·1	1·1	Nil
S.3414	Slag: Bentinck	10·95, 10·84	10·9	11·1	−0·2	4·81, 4·89	4·9	4·7	0·2
S.3415	Slag: Bentinck	16·60, 16·20	16·4	16·6	−0·2	8·19, 8·57	8·4	8·1	0·3

silicate materials since its introduction by G. SCHWARZENBACH[35]. Hopkin and Williams's monograph[33] has over 100 references to the general use of this reagent. J. BANKS[36] developed a method for silicate materials which involved the removal of iron, aluminium and titanium with ammonium hydroxide. This method was investigated and although no difficulty was experienced when standard calcium and magnesium solutions were titrated, the end points of the titrations were not consistently visible on sample solutions. The total calcium plus magnesium titration (indicator: eriochrome black) was reasonably good but the calcium titration (indicator: murexide) rarely gave a clear change from pink to purple. This difficulty is not uncommon and Shapiro and Brannock[18] constructed an automatic photometric apparatus to improve the precision of these end points.

The method finally developed closely follows that of Bennett *et al.*[14] and a series of results is compared with classical analyses in *Table 6*. No ammonia precipitation is carried out, the iron, aluminium and titanium being complexed with triethanolamine and screened indicators are used for the titrations. Experimental work was carried out to study the suitability of particular indicators and the extent of the interference of ash and slag constituents.

The mixed indicator for the titration of calcium used by Bennett *et al.*[14] is murexide and naphthol green B and this indicator was used for the calcium results shown in *Table 6*. However, since these results were obtained, calcein[30] has been found to give a more reliable end point and is now incorporated in the proposed method (see page 430: determination of calcium and magnesium). From the results obtained using standard solutions, it has been found that the true end point is not reached until the purple colour is not intensified by the further addition of EDTA solution. Supplies of calcein from two different sources have shown that the quantities in the indicator mixture may need slight adjustment to give the best colour change.

o-Cresolphthalein complexone screened with methyl red and a green dye was used by Schwarzenbach *et al.*[31] as the indicator for the titration of calcium plus magnesium. If more than 0·5 ml of a 0·1 per cent w/v solution of the indicator is used the end point tends to be from purple to a very pale grey rather than from purple to colourless. The best end points with this indicator, and with calcein, are obtained by carrying out the titrations in diffused daylight.

The effect of constituents of ash and slag on the EDTA titrations was ascertained by adding appropriate chemicals to standard calcium and magnesium solutions. The solutions were buffered in a similar manner to that specified in the proposed method. The recovery was still satisfactory with the following quantities of the various constituents: 35 per cent Al_2O_3, 70 per cent Fe_2O_3, 2 per cent Mn_3O_4, 5 per cent P_2O_5 and 5 per cent TiO_2. It was therefore concluded that almost all constituents in normal concentrations can be tolerated. Some types of boiler deposit can be relatively rich in phosphate, and would require modified treatment.

(5) *Sodium and potassium*

Flame photometric methods for the determination of sodium and potassium are now widely used in the analysis of many types of materials. Several

methods applicable to the analysis of silicate materials have been described in the literature [37–40], but when the work described here was initiated little reference to the 'Eel' flame photometer was available except for data sheets supplied by Evans Electroselenium, Ltd. P. J. JACKSON and A. C. SMITH[41] have since published a method for the determination of alkalies in coal ash and related materials.

Table 7. Comparison of methods for determining sodium and potassium

Sample No.	Description	% Na_2O				% CaO	% K_2O			
		J. L. Smith method	Mean	Flame photometer	Mean		J. L. Smith method	Mean	Flame photometer	Mean
S.3044	Ash: Thoresby	8·94, 8·98	9·0	8·52, 8·52	8·5	6·6	0·88, 1·02	1·0	0·90, 0·87	0·9
S.3045	Ash: Thoresby	5·45, 5·51	5·5	5·22, 5·15	5·2	6·3	0·57, 0·52	0·5	0·67, 0·66	0·7
S.3048	Ash: Gedling	3·72, 3·58	3·7	3·72, 3·66	3·7	2·3	1·84, 1·76	1·8	1·88, 1·86	1·9
S.3050	Ash: Clipstone	5·35, 5·28	5·3	4·98, 5·24	5·1	5·7	1·43, 1·49	1·5	1·27, 1·24	1·3
S.3053	Ash: Westthorpe	1·21, 1·35	1·3	1·15, 1·17	1·2	0·7	4·05, 3·99	4·0	4·09, 4·08	4·1
S.3066	Boiler Residue	1·89, 1·96 2·03	2·0	2·07, 2·07	2·1	11·0	2·67, 2·72 2·57	2·7	2·36, 2·34	2·4
S.3073	Ash: Langton Silkstone	1·23, 1·20	1·2	1·29, 1·27	1·3	5·5	3·37, 3·41	3·4	3·34, 3·31	3·3
S.3075	Ash: Whitwick	0·96, 0·74	0·8	0·84, 0·91	0·9	8·5	2·67, 2·85	2·8	2·36, 2·34	2·4
S.3105	Ash: Woodhorn	0·43, 0·27	0·4	0·35, 0·35	0·4	5·2	3·19, 3·23	3·2	3·10, 3·08	3·1
S.3175	Ash: Thoresby	3·39, 3·38	3·4	3·06, 3·06	3·1	9·5	2·61, 2·57	2·6	2·45, 2·43	2·4
S.3189	Ash: Cronton	0·75, 0·61	0·7	0·49, 0·49	0·5	3·8	3·66, 3·75	3·7	3·51, 3·50	3·5

From the preliminary work it was concluded that, of the elements normally present in solution B, only calcium would cause appreciable interference. This conclusion has since been confirmed by Jackson and Smith[41]. The interference of calcium is often considered to be serious, and in some methods, attempts are made to suppress its effect by adding aluminium[41] or to eliminate it by ion exchange[42]. Its effect on the sodium flame was examined using a standard calcium solution (calcium carbonate in a slight excess of 0·1N nitric acid) and the results showed an apparent increase of 0·006 per cent per 1 per cent of calcium oxide present. As the interference of calcium is reduced by the presence of aluminium and by sulphuric acid its effect may be ignored for all normal samples. Comparative results are given in *Table 7*.

Table 8. Comparison of methods for determining phosphorus and titanium

Sample No.	Description of sample	Titanium (% TiO_2)				Phosphorus (% P_2O_5)			
		Colorimetric with 'tiron'			Classical	Colorimetric as phospho-vanado-molybdate			Belcher
				Mean				Mean	
S.3066	Boiler Residue	0·86	0·88	0·9	0·8	0·34	0·33	0·3	0·4
S.3067	Boiler Residue	0·85	0·85	0·8	0·7	0·40	0·41	0·4	0·4
S.3333	Soot Ash	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0·88	0·88	0·9	0·8
S.3341	Soot Ash	1·22	1·17	1·2	1·2	*n.d.*	*n.d.*	*n.d.*	*n.d.*
S.3343	Ash: Wimblebury	0·93	0·94	0·9	0·9	0·31	0·31	0·3	0·3
S.3348	Soot Ash	*n.d.*	*n.d.*	*n.d.*	*n.d.*	1·12	1·11	1·1	0·9
S.3360	Ash: Barnsley Main	1·00	1·01	1·0	1·0	0·26	0·25	0·3	0·2
S.3368	Slag: Bentinck	0·88	0·91	0·9	0·8	0·23	0·23	0·2	0·2
S.3402	Slag: Hamstead	0·79	0·79	0·8	0·7	0·37	0·43	0·4	0·4

n.d. = not determined.

(6) *Other constituents*

The colorimetric method for determining titanium using hydrogen peroxide is classically well known, but a more sensitive method is provided by the colour developed with 'tiron'. Yoe and Armstrong[28] recommended a wavelength of 410 mμ for the optical density measurement, while Shapiro and Brannock[18] specified a wavelength of 430 mμ, probably to reduce interference from sodium dithionite to a minimum. Some results are compared with classical values in *Table 8*.

Table 9. Repeatability and accuracy of the rapid methods

Constituents	*Repeatability*			*Accuracy*			
	Standard deviation	*Degrees of freedom*	*95% limits*	*Standard deviation*	*Degrees of freedom*	*95% limits (singles)*	*95% limits (duplicates)*
1	2	3	4	5	6	7	8
SiO_2	0·186	23	±0·39	0·271	46	±0·55	±0·39
Al_2O_3	0·326	22	±0·68	0·777	44	±1·57	±1·11
Fe_2O_3	0·175	17	±0·37	0·284	35	±0·58	±0·41
CaO	0·139	34	±0·28	0·179	59	±0·36	±0·25
MgO	0·129	31	±0·26	0·268	56	±0·54	±0·38
Na_2O	0·061	11	±0·13	0·231	22	±0·48	±0·34
K_2O	0·015	11	±0·03	0·217	22	±0·45	±0·32
TiO_2	0·017	7	±0·04	0·082	14	±0·18	±0·12
P_2O_5	0·016	8	±0·04	0·088	16	±0·19	±0·13

Notes on Table 9

Column 1. The constituents Mn_3O_4 and SO_3 are not included as these determinations are well established, with an accuracy of better than ±0·1 per cent.

Column 4. These values are the 95 per cent limits for the repeatability within which a single determination would lie around the 'true result as determined by the rapid method'.

Column 5. These standard deviations are calculated for the difference between the individual rapid results and the corresponding classical result.

Column 7. These values are the 95 per cent limits for the accuracy of a single rapid result, assuming that the classical result is 'exact'.

Column 8. These values are the 95 per cent limits for the accuracy of the mean of duplicate rapid results, assuming that the classical result is 'exact'.

As the values quoted in Columns 7 and 8 include any bias of the two methods, it is clear that no serious error is introduced by making the assumption that the classical method is 'exact'. Of course the classical results are not 'exact', but they are the most convenient yardstick. A thorough survey of the accuracy for silicate analysis by classical and other methods has been reported recently by H. W. FAIRBAIRN *et al.*[45] It makes no significant difference to the values quoted in Columns 7 and 8 if, instead of assuming that the classical results are 'exact', provision is made in the statistical calculations for the classical results to be accurate to within ±0·1 per cent.

No recent experimental work has been carried out on the manganese determination as the rapid and accurate colorimetric method described has been employed for some considerable time.

The yellow phospho-vanado-molybdate method[29] is used for the determination of phosphorus. The method is exceedingly quick and simple, and the results, as shown in *Table 8*, compare favourably with the alternative rapid method of R. BELCHER[43].

Sulphur is determined gravimetrically on a separate portion of the sample as barium sulphate. The gravimetric method has been quickened by adopting more rapid filtration, precipitation and ignition techniques as used by R. A. MOTT *et al.*[44].

Table 10. Comparison of methods for the complete analysis of a coal ash, a slag and a boiler residue

Percentage of constituent	Coal ash S.3462				Slag S. 3446				Boiler residue S. 3066			
	Rapid			Class.	Rapid			Class.	Rapid			Class.
			Mean				Mean				Mean	
SiO_2	45·8	46·3	46·0	46·3	51·6	51·2	51·4	51·5	47·7	47·3	47·5	47·6
Al_2O_3	25·6	25·9	25·7	25·7	28·2	27·9	28·0	28·2	19·9	21·0	20·5	20·6
Fe_2O_3	12·39	12·31	12·4	12·2	5·36‡	5·39‡	5·4‡	5·4‡	7·40	7·43	7·4	7·4
CaO	4·55	4·60	4·6	4·8	7·75	7·79	7·8	7·9	11·16	10·70	10·9	11·1
									10·86	10·90		
MgO	2·20	2·12	2·2	2·3	1·92	1·94	1·9	2·3	3·27	3·34	3·3	3·6
Na_2O	1·52	1·53	1·5	1·6	0·42	0·42	0·4	0·3	2·07	2·07	2·1	2·0
K_2O	3·16	3·10	3·1	3·2	2·68	2·63	2·7	2·8	2·36	2·34	2·4	2·7
TiO_2	0·96	0·94	0·9	0·9	1·03	1·03	1·0	1·0	0·86	0·88	0·9	0·8
Mn_3O_4	0·19	0·17	0·2	0·2	0·17	0·18	0·2	0·1	—	—	(0·4)	0·4
SO_3	2·51	2·46	2·5	2·5	0·49	0·48	0·5	0·3	3·74	3·69	3·7	3·7
P_2O_5	0·44	0·41	0·4	0·3	0·01	0·01	<0·1	<0·1	0·34	0·33	0·3	0·4
NiO	*n.d.*	*n.d.*	*n.d.*	0·1	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
C	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0·5	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total	—	—	99·5*	100·1	—	—	99·3†	100·3	—	—	99·4	100·3

* not including NiO. † not including C. ‡ expressed as FeO.

The complete work described herein forms part of a comprehensive programme of the Analytical Department of the B.C.U.R.A. on rapid methods of inorganic chemical analysis; some aspects have come within the programmes supported by the Boiler Availability Committee and by the Ministry of Power.

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Chemical Structure of Coals: A Method for Comparing Data of Different Origins and for Testing Sets of Data for Self-consistency

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An extension of the earlier methods of statistical structural analysis has enabled a comparison to be made on a common basis between (a) *measurements on coal by X-ray diffraction, infra-red spectrometry and nuclear magnetic resonance, and* (b) *deductions by statistical structural methods from measurements of density, refractive index and heat of combustion. Unsuspected discrepancies are revealed. Structural parameters derived from measurements by the first three methods can be brought into approximate mutual agreement by making suitable and not unreasonable modifications to the structural assumptions. But the second group gives parameters that cannot be brought into agreement; these are more widely scattered and fall on both sides of those of the first group. A self-consistent set of parameters describing the variation of coal structure with rank is derived from the mathematical analysis of results from the first three methods and its implications are noted.*

ESTIMATES of numerical parameters relating to a proposed model of coal structure may refer to the same or to different features, according to the experimental method by which they were obtained. Basic chemical principles require that some of these parameters are inter-related; it should thus be possible to reduce the estimates to a common basis and so facilitate comparison between the results from different techniques. Even when the estimates refer to the same parameters, different methods may yield conflicting values and it is desirable to take further the rough appraisal of such cases made[1] by the writer in 1955.

It is unwise to compare different values of a numerical parameter from a mathematical or physical point of view alone; the chemical implications must be considered. For example, small differences in the aromatic carbon fraction[2], or the difference between 3 and 5 fused aromatic rings in a cluster, can be important when relating the structure of coal to its chemical reactions, potential reaction products and to the course of its pyrolysis. The need to choose preferred values has assumed greater importance during recent studies of the mechanism of carbonization[3] by the author, and it has become clear that the present paper must be written before this other work can be completed and adequately reported.

An early attempt[4] to inter-relate different parameters specifying the average coal molecule, using chemical principles, was found inadequate for this purpose and at the same time shortcomings, evident below, were found in the application of methods developed[5] by D. W. VAN KREVELEN. Further work was therefore undertaken in order to develop means for:

(*a*) assessment of the self-consistency of structural data,
(*b*) interconversion of structural parameters, and
(*c*) selection if possible of a self-consistent set of parameters lying within the experimental errors of all the available estimates.

The methods developed in this paper can detect inconsistencies in the data provided that the fundamental assumption on which they are based, an aromatic/aliphatic/alicyclic model of coal of the type proposed by D. W. VAN KREVELEN[6] and illustrated—for example—by the writer[3], is correct. Though this is the simplest likely model in the present state of knowledge, and supported by much of the infra-red and x-ray evidence, it is not universally accepted[7]. And if, for example, 7-carbon aromatic rings were present some of the tests developed and parameters used would have to be modified.

PRINCIPLES OF METHOD

The parameters now mainly used to describe coal structures of the type envisaged—see the glossary for their definitions—are: R_a, C_{ar}, $2(R_a - 1)/C'_{ar}$; f_a, $H'_{ar}/H'_{al+alic}$; B, and H'_1/C'. Two independent parameters are needed to specify the average cluster unit: one from the first group of three (which, subject to shape of aromatic system, are equivalent), and one from the next group of two (which, subject to minor uncertainties, are equivalent). B is a third independent parameter relating to the whole molecule. H'_1/C' is determined by the three independent parameters and can be estimated by chemical analysis; it can therefore by used as a means for computing any one of the independent parameters in terms of the other two.

In application the procedure differs for each set of data according to the parameter specified. But whichever of the cluster parameters is given, the remainder can be calculated independently of assistance from other experimental evidence apart from ultimate analysis provided B can be estimated or assumed. This contrasts with the procedure so far adopted: e.g. van Krevelen[5] found it necessary to use values of C_{ar} from refractometric data and values of f_a from densimetric data in order to calculate a complete set of parameters; and J. K. BROWN and P. B. HIRSCH[8] combined x-ray and infra-red data with the same general intention. By the present method it becomes possible to test whether, for example, the two parameters deduced by van Krevelen are compatible (as assumed in his own treatment) and whether P. B. HIRSCH's data[9] are in fact compatible with those of J. K. BROWN[10]—as they, also, assumed.

Moreover if two parameters, one from the ring-number group and one from the aromaticity group, are both experimentally determined, an internal consistency test can be applied; if they prove to be inconsistent the test also provides a numerical factor that can be used to correct one or both. This case has not yet arisen with the experimental sets of data, but the correction has been applied to a mean set of parameters thought to provide the best estimates yet available.

Development of the key equations

Equation (2) in an earlier paper[11] relating the ring condensation index, the hydrogen/carbon ratio after correction for oxygen, and the fraction of

carbon in aromatic form has been re-stated more precisely by van Krevelen and Schuyer (ref. 5, p 146) as follows

$$2(R-1)/C' = 2 - f_a - (H'/C') - (B/C') \quad \ldots . [1]$$

In earlier papers on this subject, because R was thought to be large, the term B/C' was considered negligible and omitted. Estimates of R by all methods have continued to fall, and inclusion of B/C' is now essential if the equation is to have any value; but unfortunately the value of B/C' cannot be estimated in advance of those of the other parameters. Van Krevelen has therefore been unable to use the revised equation, and has claimed incorrectly (ref. 5, p 146) that the omission of B/C' gives average values of the other parameters for the whole molecule; but on the contrary, it gives meaningless values[2]. The difficulty is circumvented here by abandoning the use of equation 1 and adopting an alternative method for achieving the same end.

The corrections for oxygen-containing groups, applied in all previous work, were intended to convert the coal structure in effect to the equivalent hydrocarbon structure. This process can be carried further. Aliphatic chains and bridges can be replaced by hydrogen at the points where they join the aromatic nuclei, and direct links between carbon atoms in different nuclei can similarly be eliminated. This involves some consideration of the forms of aliphatic and alicyclic groups likely to be present in coals and an estimation of values of the linkage number B. In previous work these processes have not been clearly envisaged as a whole, but a unified treatment is now attempted. One thus obtains parameters for the average cluster unit nucleus after conversion to the parent aromatic hydrocarbon. A much-simplified form of equation 1 is then applicable since f_a has the value unity and B/C' has been eliminated

$$2(R_a - 1)/C'_{ar} + H'_{aru}/C'_{ar} = 1 \quad \ldots . [2]$$

In this equation H'_{aru} refers to the number of hydrogen atoms remaining in the average cluster unit after all substituent groups and linkages have been replaced by hydrogen: it is the hydrogen in the aromatic skeleton when un-substituted.

The next step is to calculate H'_{aru}/C'_{ar}. This can be done with the help of the equation on page S30 of reference 12; the term in square brackets represents an approximation to $(H'_{aru} - B_0)/C'$ when alicyclic rings are absent (but neglecting the oxygen corrections), and lower on the same page it is shown that the addition of the term $\frac{1}{4}(1 - f_a - f)$ allows for the presence of alicyclic rings also. The first term in the square brackets is equal to H'_{ar}/C', the second to the number of aliphatic chains or bridges leading from an average cluster nucleus. Thus

$$\frac{H'_{aru} - B_0}{C'} = \frac{H'_{ar}}{C'} + \frac{f}{n} + \frac{1}{4}(1 - f_a - f) + \text{oxygen correction} \quad \ldots . [3]$$

Now

$$H'_{ar} = H'_0 - k\,C'(1 - f_a) \quad \ldots . [4]$$

where k is the average atomic ratio of non-aromatic hydrogen to non-aromatic carbon in the molecule and

$$\text{oxygen correction} = (H_1' - H_0')/C' \quad \ldots . [5]$$

Therefore

$$\frac{H'_{aru} - B_0}{C'} = \frac{H_1'}{C'} - k(1 - f_a) + \frac{f}{n} + \frac{1}{4}(1 - f_a - f) \quad \ldots . [6]$$

At this stage there are two alternatives: to treat the (unknown) number of aliphatic bridges as aliphatic chains and to correct for inter-cluster linkages (B_0) only in respect of direct C—C bonds between aromatic nuclei; or to correct only for aliphatic chains leaving the bridges to be dealt with as part of the linkages B. The second method was adopted since there is no information about the proportion of direct inter-nuclear C—C bonds. The difficulty still remains that the proportions of non-aromatic hydrogen in the forms of chains, bridges and alicyclic rings are not known; but fortunately this is of minor importance as the following analysis shows.

The supposition (*a*) that all the non-aromatic groups are in the form of chains leads to equation 7 (this and the second supposition are most unlikely since the inter-cluster linkages would then be entirely between nuclear carbon atoms and for steric reasons the chains and buckled alicyclic rings could scarcely be accommodated); (*b*) that all non-aromatic groups are alicyclic, to equation 8; and (*c*) that all are bridges, again to equation 7.

(*a*) $B_0 = B, \quad f = 1 - f_a, \quad k = 2 + 1/n;$
$\therefore (H'_{aru} - B)/C' = (H'/C') - 2(1 - f_a) \quad \ldots . [7]$

(*b*) $B_0 = B, \quad f = 0, \quad k = 2;$
$\therefore (H'_{aru} - B)/C' = (H_1'/C') - 1{\cdot}75(1 - f_a) \quad \ldots . [8]$

(*c*) $B_0 \neq B, \quad f = 1 - f_a, \quad k = 2;$
$\therefore (H'_{aru} - B_0)/C' = (H_1'/C') - 2(1 - f_a) + (1/n)(1 - f_a)$

But in this case it was decided (above) to correct for aliphatic bridges via the B term; hence here also we put $B_0 = B$, and delete the last term*. This leads again to equation 7.

Since an appreciable proportion of the non-aromatic material is alicyclic[13], the correct relation lies somewhere between equations 7 and 8. A mean between these has therefore been adopted.

$$(H'_{aru} - B)/C' = (H_1'/C') - 1{\cdot}875(1 - f_a) \quad \ldots . [9]$$

Since $C'_{ar} = f_a C'$

$$(H'_{aru} - B)/C'_{ar} = 1{\cdot}875 - (1{\cdot}875 - H_1'/C')/f_a \quad \ldots . [10]$$

Equation 7 is similar to equation 10 in an early paper[4], which however included alicyclic carbon in the ring nucleus whose hydrogen/carbon ratio was sought.

* It has been checked that treatment of a typical molecule in these alternative ways leads, through the application of the above formulae or their equivalent, to the same result.

Oxygen corrections to H'/C'

If the reasonable assumption is made[3] that hydroxyl oxygen amounts to 60 per cent of the total in a bright coal, the remaining 40 per cent must be split between quinone, ether and heterocyclic forms. The amount in ether and heterocyclic forms is small, and inappreciable error is caused by bracketing these as ether; if an ether oxygen atom links two clusters it must be replaced by two hydrogen atoms, one on each cluster; if within a single cluster (e.g. methoxy), no hydrogen correction is necessary on elimination; little error is introduced by assuming equal division of ether between these two cases, and thus replacing one ether oxygen by one hydrogen atom. Since quinone oxygen is also replaced by one hydrogen atom, the whole of the 40 per cent non-hydroxyl oxygen can be thus treated; the fact that estimates of quinone content have recently increased[14] therefore makes no difference. To the hydrogen content of the coal must thus be added 1/16th of 40 per cent of the oxygen content, i.e.

$$H_1 = H + 0{\cdot}025\ O \qquad \ldots . [11]$$

It is important to note the following definitions. H_0 is the hydrogen content after subtraction of hydroxyl hydrogen, i.e.

$$H_0 = H - 0{\cdot}0375\ O \qquad \ldots . [12]$$

This is used when calculating aromatic and non-aromatic hydrogen from, say, the ratios given by infra-red spectroscopy, but the correction is not made when using the main formulae of this paper because the numbers of hydrogen atoms in a phenol and the parent hydrocarbon are identical. In these main formulae the value H_1, obtained after compensating for all oxygen groups (equation 11), is used.

Inter-cluster linkages

Whether clusters are linked linearly or in raft-like formation, the inner clusters will have more connections to others than those that terminate the molecule. Suppose that the average number leading from an inner cluster is equal to $2l$ and that the molecule contains m clusters; then the number of hydrogen atoms per cluster to be added if these inter-linkages are broken is by definition equal to B and equals $2l(m-1)/m$. Since the inner clusters are linked at least singly to each of two others, $l \not< 1$; it cannot be $\gg 1$ because of the steric strain that would be involved; therefore l is likely to be slightly greater than unity, probably increasing slightly as m increases. If $m > 4$, $B \gtrsim 2$; if $m = 2$, $B = 1+$; the limits of B may be set at $1\frac{1}{2}$ to $2\frac{1}{2}$ with a most likely value of 2.

Other relations between parameters and final estimation of H'_{aru}/C'_{ar}

Since some experimental methods lead to values for the ring condensation index, others to C'_{ar}, and others to f_a, certain further relations are necessary before equations 2 and 10 can be applied. Relations between $2(R_a - 1)/C'_{ar}$, R_a, C'_{ar} and H'_{aru} can be obtained graphically from the mathematical properties of model molecules for the two extreme shapes, pericondensed and catacondensed[15] (*Figures 1* to *3*). It is also necessary to estimate H'_{aru} itself, by

successive approximation using one of these relations (*Figure 3*), during the final calculation of H'_{aru}/C'_{ar} from equation 10. The term on the LHS of equation 10 is subtracted from unity (equation 2) and the result taken as a first approximation to $2(R_a - 1)/C'_{ar}$. The corresponding value of H'_{aru} is then read from *Figure 3* and the term on the LHS corrected accordingly [multiplied by $H'_{aru}/(H'_{aru} - B)$ where $B \sim 2$]. This procedure is repeated until

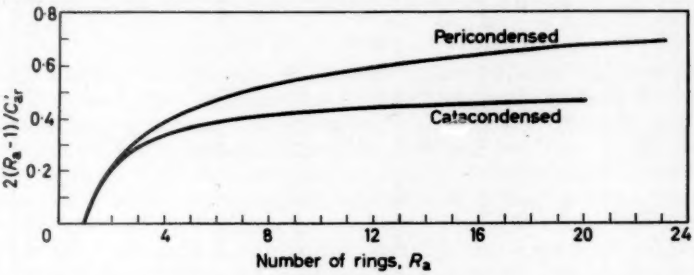


Figure 1. Ring condensation index of polycyclic aromatic systems in relation to number of rings

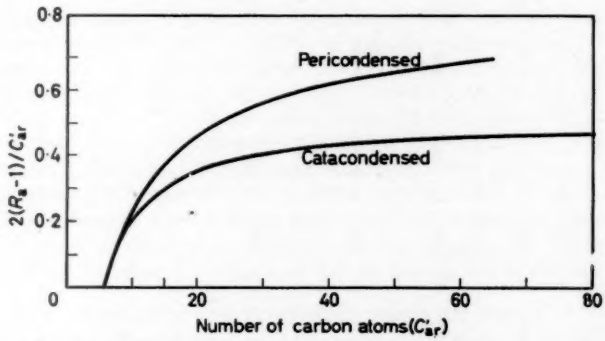


Figure 2. Ring condensation index of polycyclic aromatic systems in relation to carbon atoms

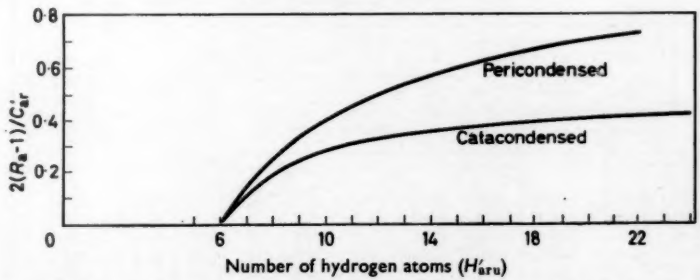
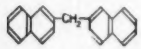
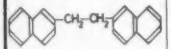


Figure 3. Ring condensation index of polycyclic aromatic systems in relation to hydrogen atoms

Table 1. Model compounds

Compound	Quantities (average per cluster) derived directly from the chemical formula												Quantities estimated from equations in text					Remarks
	R	R_a	B	H_i'	C'	$\frac{H_i'}{C'}$	C_{ar}'	f_a	H_{aru}'	$\frac{2(R-1)}{C'}$	$\frac{2(R_a-1)}{C_{ar}'}$	$\frac{H_{aru}'}{C_{ar}'}$	$[f_a]$*	$\frac{H_{aru}}{C_{ar}'}$ †	$\frac{2(R_a-1)}{C_{ar}'}$ ‡	R_a §	C_{ar}' ‖	
	2	2	0	8	10	0·80	10	1·00	8	0·20	0·20	0·80	1·00	0·80	0·20	Peri Cata 1·95 2·05	Peri Cata 9·5 10	
	2	2	0	10	11	0·91	10	0·91	8	0·18	0·20	0·80	0·91	0·815	0·185	1·85 1·95	9 9·5	
	2	2	1	7	10	0·70	10	1·00	8	0·20	0·20	0·80	1·10	Peri Cata 0·81 0·80	Peri Cata 0·19 0·20	1·9 2·1	9 10	Note impossible value of $[f_a]$
	2	2	1	8	10·5	0·76	10	0·95	8	0·19	0·20	0·80	1·05	0·81 0·80	0·19 0·20	1·9 2·1	9 10	Note impossible value of $[f_a]$
	2	2	1	9	11	0·82	10	0·91	8	0·18	0·20	0·80	1·00	0·83 0·82	0·17 0·18	1·8 1·9	8·5 9·5	
Hypothetical molecular model which may resemble coal [J. Inst. Fuel 30 (1957) 193]	3·25	3·0	2·5	13·75	17	0·81	13·25	0·78	9·5	0·265		0·715	0·925	0·735 —	0·265 —	2·45 —	11 —	$B=2$ would (increase R_a (estimated). $[f_a]-B/C'=0·78$ if $B=2·5$, 0·81 if $B=2$; good agreement with f_a

* $[f_a]$ from equation 1 assuming $B = 0$, i.e. an estimate of f_a that is incorrect when cluster units are interlinked.
† from equation 10; using value of B and successive approximation when $B \neq 0$.
‡ from equation 2 and previous column.
§ from *Figure 1* and previous column.
‖ from *Figure 2* and $2(R_a-1)/C_{ar}'$ column.

the values no longer change. The final result is the correct estimate of H'_{aru}/C'_{ar}.

From a knowledge of the uncertainty of the experimental estimates and of the assumptions made it is possible to place limits on each series of calculated parameters so that it can be seen whether disagreement between experimental methods is absolute or within the possible error. Details of procedure, which vary from method to method, will emerge in the later sections.

APPLICATION TO MODEL COMPOUNDS

Table 1 shows for certain model substances how parameters derived from quantities such as can be determined even for coals, by the methods developed in the preceding section, and for the two extreme types (pericondensed and catacondensed) of aromatic condensation, compare with their actual values. The calculated number of aromatic rings and of aromatic carbon atoms per cluster unit, and the ring condensation index, may deviate (usually negatively for the pericondensed shape) by some 10 per cent from the true values. *Table 1* also illustrates how incorrect (high) can be the estimate of f_a from equation 1 when the term B/C' is ignored; its inclusion brings the derived and true values into close agreement. Conversely the omission of B/C' by D. W. VAN KREVELEN and J. SCHUYER[5] when calculating the ring condensation index from f_a (deduced from densities of coals) leads to values of the index that are approximately 0·1 unit too high, so that the ring numbers tend to be 1 to 3 units too high. Naturally the method works least well with the complicated hypothetical structure but even in this case a ring number within half a unit (20 per cent) of the correct one is indicated. One reason for the greater deviation with the hypothetical structure is that the values of R_a, C'_{ar}, C' and H'_1 have been taken as the arithmetic means of those for the four cluster units, whereas if the equations in the previous section are to apply precisely the hydrogen/carbon ratio and the ring condensation index, rather than the values of their component parameters, should be averaged. Consequently the R_a values deduced for coals will not be exactly the arithmetic means.

COMPOSITION OF COALS USED FOR COMPARISONS

It is important to make comparisons over a considerable range of rank. Since, however, the properties of any single coal are likely to deviate from

Table 2. Analyses assumed for 'average' bright coals

Coal No.	*Probable N.C.B. Rank Coding No.*	*Analysis, % d.m.f. (Parr basis)*					H_0* %	H_1† %	H'_1/C' (atomic)	O'/C' (atomic)	% d.a.f. C
		VM	*C*	*H*	*N*	*O + errors*					
1	702	38·8	82·5	5·3	1·8	10·4	4·91	5·56	0·805	0·095	81·7
2	501	35·4	85·0	5·3	1·8	7·9	5·00	5·50	0·77	0·069	84·2
3	401	31·0	87·5	5·2	1·8	5·5	5·00	5·34	0·73	0·047	86·6
4	301	24·4	90·0	4·9	1·7	3·4	4·77	4·99	0·66	0·028	89·1
5	201	13·5	92·5	4·15	1·25	2·1	4·07	4·20	0·54	0·017	91·6

H_0*: $H_0 = H - 0{\cdot}0375\,O$ $\qquad$ H_1†: $H_1 = H + 0{\cdot}025\,O$

‡ from equation 2 and previous column.
§ from *Figure 1* and previous column.
‖ from *Figure 2* and $2(R_a-1)/C_{ar}$ column.

* f_a from equation 1 assuming $B = 0$, i.e. an estimate of f_a that is incorrect when cluster units are interlinked.
† from equation 10; using value of B and successive approximation when $B \neq 0$.

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the mean coalification line and most investigators have examined only a few coals it appears preferable when comparing results to take smoothed values from the curves of each investigator at a limited number of standard d.m.f. carbon contents. The 'average' bright coals as defined by the writer previously[4] have therefore been chosen but, to remain more completely in the experimental range, the limits have been reduced and intermediate 'coals' inserted so that the series covers carbon contents from 82·5 to 92·5 per cent in five steps (*Table 2*). The values of H_0 and H_1 (corrected for oxygen groups) are included and were used as described above (p 448).

The values of H_0 and H_1 are shown (unjustifiably) to two places of decimals so that the final rounding off of ratios and other derived quantities can be effected to the degree warranted by the observations.

APPLICATION TO AVAILABLE DATA FOR COALS

The available results have been plotted against rank for each method considered, and the relevant information for the standard coals described in the previous section taken from the smoothed curves. Results can be classified broadly into those that yield, directly or after preliminary calculations, values of the fraction of carbon in aromatic form (these methods are infra-red spectroscopy, nuclear magnetic resonance, and density in relation to elementary composition) and those that yield parameters related to the size of aromatic nuclei (these are x-ray diffraction, molecular refraction in relation to elementary composition, and calorific value in relation to composition). The order of presentation follows this classification. The order of columns in the tabulated results follows for simplicity the sequence of calculation and therefore differs for each method; the key results, however, are later collected for comparison (see *Table 13*).

Infra-red spectroscopy: results of J. K. Brown[10]

The basic measurements reported by Brown concern the ratio of the optical densities of two neighbouring absorption peaks in the spectra of coals, at 3 030 and 2 920 cm^{-1}, respectively assigned to aromatic and non-aromatic C—H stretching vibrations. Because of the closeness of these peaks the error in the base line from which measurement was made was assumed to be negligible. Experimental determinations were also made on selected araliphatic compounds; the ratio $H_{ar}/H_{al+alic}$ was found to equal from one to three times the observed optical density ratio. Brown therefore used an average value of 2 when interpreting his results on coals, but in the present paper it is necessary to consider the possible values 1, 2 and 3. Brown and Hirsch[8] proceeded to calculate first the percentage of aliphatic and alicyclic hydrogen in the coals from the sum (i.e. the total hydrogen less that in the form of hydroxyl) of this and the aromatic hydrogen in conjunction with the above ratio; then the carbon in this form on the assumption that there was one carbon per two hydrogen atoms; then the carbon in aromatic form by difference from the total carbon content; and thus finally the fraction of carbon in aromatic form.

In the present paper this fraction (f_a), similarly calculated from Brown's curve of optical density ratios at the d.m.f. carbon contents of the 'average'

coals, forms the starting point of the mathematical analysis leading to values of R_a; the hydroxyl correction has been calculated on the assumption that 60 per cent of the total oxygen in coals is hydroxyl oxygen (see H_0 in *Table 2*) and the weight factor for converting non-aromatic hydrogen to non-aromatic carbon has been taken as 12/2·1 consistently in all methods, in order to allow for a small number of methyl groups as indicated by the spectra. The differences from the calculations of Brown and Hirsch caused by these modifications are small compared with those introduced by using the three conversion factors (1, 2 and 3) in place of Brown's single factor of 2. The results starting from the 'experimental' estimates of f_a are collected in *Table 3*.

Table 3. Results from i.r. spectroscopy (J. K. BROWN[10])

Coal No.	*C, d.m.f.* %	$\frac{H_{ar}/H_{al+alic}}{D_{3030}/D_{2920}}$	f_a	$\frac{H'_{aru} - B}{C'_{ar}}$ (*from eqn 10*)	$\frac{H_{aru}}{C'_{ar}}$ (*assuming B=2*)	$\frac{2(R_a-1)}{C'_{ar}}$ (*from eqn 2*)	R_a (*from Figure 3*)
1	82·5	1	0·695	0·34	0·39	0·61	13·0
2	85	1	0·70	0·30	0·34	0·66	18·5
3	87·5	1	0·725	0·295	0·33	0·67	19·5
4	90	1	0·765	0·28	0·31	0·69	23·0
5	92·5	1	0·845	0·295	0·33	0·67	19·5
1	82·5	2	0·725	0·40	0·475	0·525	8·0
2	85	2	0·73	0·365	0·425	0·575	10·6
3	87·5	2	0·76	0·365	0·425	0·575	10·6
4	90	2	0·805	0·365	0·425	0·575	10·6
5	92·5	2	0·89	0·375	0·435	0·565	9·9
1	82·5	3	0·75	0·45	0·55	0·45	5·5
2	85	3	0·76	0·42	0·505	0·495	6·8
3	87·5	3	0·79	0·425	0·51	0·49	6·7
4	90	3	0·835	0·42	0·505	0·495	6·8
5	92·5	3	0·915	0·415	0·50	0·50	7·0

Estimates of H'_{aru}/C'_{ar} (by successive approximation) could only be obtained for the pericondensed shape of ring system and for this reason there are no results for the catacondensed shape in *Table 3*.

Nuclear magnetic resonance: results of R. E. RICHARDS et al.[16]

Richards *et al.* have published ratios (r_0) that should approximately represent $H_{ar}/H_{al+alic}$ for three coals. These published results must be corrected for the hydroxyl content of the coals since hydrogen attached to oxygen probably behaves like aromatic hydrogen in this technique

$$r = r_0 - (1 + r_0)(H_{OH}/H) \quad \ldots . [13]$$

A further uncertainty arises since the hydrogen of methyl groups in the *peri* position (or otherwise in close proximity) gives a contribution to the 'second moment' (mean square width of the resonance line) approaching that of hydrogen in methylene groups and much larger than that of aromatic hydrogen, whereas that of other methyl groups can scarcely be distinguished

from the contribution of aromatic hydrogen. If it is assumed* that the ratio of non-aromatic hydrogen in methyl to that in methylene is of the order of 1 : 10, upper and lower limits can be calculated in which respectively all or none of the methyl groups are in the *peri* position:

Upper limit : r
Lower limit : $0{\cdot}9\ (r - 0{\cdot}11)$

In view of these preliminary modifications to the published data this stage of the calculation is summarized in *Table 4*.

Table 4. Values of $H_{ar}/H_{al+alic}$ from n.m.r.: corrections for hydroxyl and peri-*methyl*

Coal, % C	*As published*[16]	*Corrected for hydroxyl*	*Corrected for* peri-*methyl*	
			Upper limit	*Lower limit*
79·2	0·5	0·36	0·36	0·23
83·1	0·8	0·69	0·69	0·52
92·6	1·8	1·74	1·74	1·46

In the absence of definite information in the publications it was assumed that the carbon contents of the coals used were on the d.m.f. basis according to King, Maries and Crossley; this, since the analysis includes organic sulphur, is roughly equivalent for low ash coals to a d.a.f. basis. The results were then plotted against carbon content and values of the hydrogen

Table 5. Results from nuclear magnetic resonance (R. E. RICHARDS[16])

Coal No.	*C, d.m.f.* %	*Basis*	f_a	$\frac{H'_{aru} - B}{C'_{ar}}$	$\frac{H'_{aru}}{C'_{ar}}$	$\frac{2(R_a - 1)}{C'_{ar}}$	R_a
1	82·5	*Upper limit*	0·78	0·50	0·63	0·37	3·8
2	85	*Upper limit*	0·815	0·52	0·665	0·335	3·2
3	87·5	*Upper limit*	0·84	0·51	0·65	0·35	3·5
4	90	*Upper limit*	0·87	0·48	0·60	0·40	4·3
5	92·5	*Upper limit*	0·905	0·40	0·475	0·525	8·0
1	82·5	*Lower limit*	0·76	0·47	0·585	0·415	4·7
2	85	*Lower limit*	0·79	0·475	0·59	0·41	4·5
3	87·5	*Lower limit*	0·82	0·48	0·60	0·40	4·3
4	90	*Lower limit*	0·855	0·45	0·55	0·45	5·5
5	92·5	*Lower limit*	0·895	0·385	0·455	0·545	9·0

ratio for each of the five standard coals (*Table 2*) taken from the smoothed curves. From these, values of f_a were calculated exactly as with the results from infra-red spectroscopy, and these formed a starting point for the mathematical analysis (*Table 5*). Results based on the assumption of catacondensed aromatic systems were again unobtainable.

* Private communication, J. K. Brown: not derived from quantitative measurement.

Statistical structural analysis (densimetric method): results of D. W. VAN KREVELEN et al.[5]

Van Krevelen *et al.* have derived values of f_a from a master-plot relating molecular volume per carbon atom and hydrogen/carbon ratio for known araliphatic hydrocarbons. These were read off from their curve at the d.a.f. carbon contents of the standard coals since the analyses included sulphur. From this point analysis by the present methods was carried forward exactly as with the values of f_h derived from spectroscopy and magnetic resonance. For the two coals of lowest rank values for catacondensed systems were obtainable. Results are summarized in *Table 6.*

Table 6. Results from densimetric analysis (D. W. VAN KREVELEN et al.[5])

Coal No.	*C, d.m.f. %*	f_a	$\frac{H'_{aru}-B}{C'_{ar}}$	$\frac{H'_{aru}}{C'_{ar}}$ (*if* $B=2$)		$\frac{2(R_a-1)}{C'_{ar}}$		R_a	
				Peri	*Cata*	*Peri*	*Cata*	*Peri*	*Cata*
1	82·5	0·83	0·59	0·805	0·76	0·195	0·24	2·0	2·4
2	85	0·845	0·57	0·765	0·69	0·235	0·31	2·2	3·3
3	87·5	0·865	0·55	0·725	—	0·275	—	2·5	—
4	90	0·89	0·51	0·65	—	0·35	—	3·5	—
5	92·5	0·93	0·44	0·535	—	0·465	—	5·9	—

X-Ray diffraction: results of P. B. HIRSCH[9]

Hirsch and his colleagues have deduced the average diameters of the ordered systems (laminae) in the coal molecule, the frequency distributions of these diameters, and a 'percentage of amorphous material' whose significance is not very clear. They have correlated the diameters of laminae with the numbers of carbon atoms in the ordered systems and it is the estimates of this quantity C'_0 (N in Figure 4 of ref. 9) that have been used for the purpose of this paper. Hirsch's carbon contents being KMC d.m.f. values, the quantities used here were read from this figure at the standard coal d.a.f. values of carbon.

Accepting the significance attached by Hirsch to the number of atoms thus estimated, values for C'_{ar}, and thus of $2(R_a-1)/C'_{ar}$ from *Figure 2*, can be calculated as follows.

Quinone and phenolic hydroxyl oxygen atoms will both contribute to the layer size to a slightly greater extent than the corresponding number of carbon atoms; since there is not much oxygen in other forms there can be little error therefore in assuming all the oxygen atoms in a cluster unit to be included in C'_0. If the alicyclic rings occur singly, then since those carbon atoms in aliphatic chains and alicyclic rings that are attached directly to the aromatic rings will contribute fully to the layer size,

$$C'_0 = C'_{ar} + C'f/n + \tfrac{1}{2}C'(1-f_a-f) + O'$$
$$= \tfrac{1}{2}C'[f_a + 1 + 2O'/C' + f(2/n-1)] \quad \ldots . [14]$$

If all non-aromatic carbon is aliphatic, then

$$C'_0 = \tfrac{1}{2}C'[f_a + 1 + 2O'/C' + (1 - f_a)(2/n - 1)] \quad \ldots . [15]$$

If all is alicyclic, *or* if n has the very likely average value of 2, then

$$C_0 = {}_2C'(f_a + 1 + 2O'/C') \quad \ldots . [16]$$

Values of C' estimated from equations 15 and 16 are unlikely to differ by more than 5 per cent at most. Little error will therefore be introduced if we use equation 16. Therefore

$$C'_{ar} = f_aC' = 2C'_0/[1 + \{1 + 2O'/C'\}/f_a] \quad \ldots . [17]$$

These values of C'_{ar} form the starting point of the analysis in this paper. With the aid of *Figure 2* they lead to values of $2(R_a - 1)/C'_{ar}$.

The difficulty in using equation 17 is that f_a could not be determined by Hirsch. Hence it has been necessary to plot, for each coal, calculated values of $2(R_a - 1)/C'_{ar}$ against assumed values of f_a. Different curves of this type were also obtained in the following manner.

H'_{aru}/C'_{ar} can be calculated as a function of f_a for each coal using equation 10 and *Figure 3*; from this, by subtraction from unity, $2(R_a - 1)/C'_{ar}$ can be obtained and plotted against f_a. Curves derived by the first and second methods will intersect (in practice almost at right angles) and the points of intersection yield unique and self-consistent values of the ring condensation index and of f_a, and hence of the other related parameters. The curves are not reproduced here and *Table 7* contains only the final results. For only one coal was it possible to obtain estimates corresponding to catacondensed aromatic systems.

Table 7. Results from X-ray diffraction (P. B. HIRSCH[9])

Coal No.	*C, d.m.f. %*	C'_0	$\frac{2(R_a - 1)}{C'_{ar}}$		f_a		C_{ar}	
			Peri	*Cata*	*Peri*	*Cata*	*Peri*	*Cata*
1	82·5	15·4	0·30	0·265	0·80	0·825	12·5	12·5
2	85	16·3	0·335	—	0·815	—	13·5	—
3	87·5	16·7	0·36	—	0·835	—	14·5	—
4	90	17·2	0·38	—	0·88	—	15·5	—
5	92·5	18·4	0·415	—	0·95	—	17·5	—

Statistical structural analysis (refractometric method): results of D. W. VAN KREVELEN et al.[5]

By using an independently developed correlation[17] van Krevelen and Schuyer have derived values of C'_{ar} from measurements of molecular refraction. The basic quantity derived from the measurements was f_aI_M/C'_{ar}. Van Krevelen

then made use of the densimetric estimate of f_a to calculate I_M/C'_{ar} and hence the aromatic surface and C'_{ar}. But in the present method it was necessary to be independent of densimetric estimates. Hence an assumed value of f_a was used to obtain a first approximation to I_M/C'_{ar} and thus C'_{ar}. From *Figures 2* and *3* estimates of the ring condensation index, R_a, and of H'_{aru} can then be obtained; H'_{aru}/C'_{ar} can be calculated from equation 2 and data are thus available for the calculation of $(H'_{aru} - B)/C'_{ar}$ when $B = 2$. This by the use of equation 10 in reverse yields a revised estimate of f_a. Successive approximations give consistent values leading to an unequivocal value of C'_{ar}.

It was first necessary to apply this process to van Krevelen's three actual coals, Nos. 2, 3 and 4 of ref. 5 (in his original paper his coals 1 to 4 fell in line with the point for graphite at the origin on the plot corresponding to Fig. VII.10 of ref. 5, but in the book—where higher densimetric estimates of f_a are used—only his coals 2 to 4 fell on this line). When this new method was applied it was found that only van Krevelen's coals 3 and 4 fell in line with graphite and that separate lines were obtained for the 'pericondensed' and 'catacondensed' assumptions. These two coals are in the bituminous range, however, and following the principle established by van Krevelen the slopes of these lines were used to establish the equations:

$$C'_{ar} = 398/(100 - C) \text{ (peri)} \quad \ldots . [18]$$

and

$$C'_{ar} = 346/(100 - C) \text{ (cata)} \quad \ldots . [19]$$

corresponding to equation VII.30 of ref. 5. From these equations, using the d.a.f. carbon contents of coals Nos. 1 to 5 defined in this paper, the values of C'_{ar} for these coals were calculated, and from these by the above procedure the other parameters were derived.

In this case complete sets of estimates for both peri and catacondensed systems were obtainable. Results are shown in *Table 8.*

Table 8. Results from refractometric analysis (D. W. VAN KREVELEN *and* J. SCHUYER[5])

Coal No.	*C, d.m.f. %*	C'_{ar}		$\frac{2(R_a - 1)}{C'_{ar}}$		$\frac{H'_{aru}}{C'_{ar}}$		$\frac{H'_{aru} - B}{C'_{ar}}$		f_a		R_a	
		Peri	*Cata*	*Peri*	*Cata*	*Peri*	*Cata*	*Peri*	*Cata*	*Peri*	*Cata*	*Peri*	*Cata*
1	82·5	21·7	18·9	0·475	0·34	0·525	0·66	0·435	0·555	0·745	0·81	6·3	4·1
2	85	25·1	21·9	0·515	0·36	0·485	0·64	0·405	0·55	0·75	0·835	7·6	4·8
3	87·5	29·7	25·8	0·55	0·385	0·45	0·615	0·385	0·54	0·77	0·86	9·2	6·1
4	90	36·5	31·8	0·59	0·405	0·41	0·595	0·355	0·53	0·80	0·90	11·6	7·5
5	92·5	47·1	41·0	0·645	0·43	0·355	0·57	0·315	0·525	0·855	0·99	16·7	10·1

Statistical structural analysis (*heat of combustion*)*: results of* I. G. C. DRYDEN *and* M. GRIFFITH[18]

Dryden and Griffith used correlations of M. KHARASCH[19] to derive estimates of $2(R_a - 1)/C'$ directly. If f_a were known the analysis by the present methods

could be carried forward exactly as from the corresponding point with the refractometric method[5]. But since f_a was not known, successive approximation had to be used: first assuming that f_a was unity; then dividing the value of $2(R_a - 1)/C'$ by the first estimate of f_a thus obtained, in order to get a second approximation to $2(R_a - 1)/C'_{ar}$; and so on. Values for catacondensed systems were unobtainable. Results are summarized in *Table 9*.

Table 9. Results from heats of combustion (I. G. C. DRYDEN *and* M. GRIFFITH[18])

Coal No.	*C, d.m.f.* %	$\frac{2(R_a - 1)}{C'}$	f_a	$\frac{2(R_a - 1)}{C'_{ar}}$	$\frac{H'_{aru} - B}{C'_{ar}}$	$\frac{H'_{aru}}{C'_{ar}}$ (*if* $B=2$)	R_a
1	82·5	0·415	0·71	0·585	0·36	0·415	11·2
2	85	0·44	0·72	0·61	0·34	0·39	13·0
3	87·5	0·465	0·74	0·63	0·325	0·37	15·0
4	90	0·50	0·78	0·64	0·315	0·36	16·0
5	92·5	0·565	0·845	0·67	0·295	0·33	19·5

EFFECTS OF VARYING THE ASSUMPTIONS MADE

The comparative mathematical analyses of data, made in the previous sections, all depend upon assumptions as to relative concentrations of different oxygen groupings, the mean factor 1·875 in equation 10, and the value of 2 for B (the inter-cluster linkage factor). It is now necessary to consider to what extent changes of these quantities affect the derived results and in particular whether better agreement can be secured using values different from those chosen above.

Estimates of quinone groups in coal have recently been increased[14] but this does not affect the oxygen correction to hydrogen/carbon ratio. The limits of oxygen as hydroxyl may be taken as 80 per cent and 40 per cent of the total oxygen instead of the 60 per cent so far assumed. These limits will affect correspondingly the values of H_1 and H_0 in *Table 2*, and thus various steps in all the calculations made.

In the section on inter-cluster linkages the likely limits of B were shown to be 1·5 to 2·5. The factor 1·875 in equation 10 involves the assumption that non-aromatic carbon is distributed equally between aliphatic (chain and bridge) and alicyclic forms; if all were in the first form the factor would be 2·0 and if all in the second, 1·75. An experiment of W. F. WYSS (quoted by I. G. C. DRYDEN[13]) may be taken to give a lower limit for alicyclic hydrogen and thus carbon, while the low intensity of the infra-red peak for methyl hydrogen gives a lower limit for the aliphatic material. The permissible limits for the factor may therefore be set at 1·8 and 1·95, corresponding to 80 per cent and 20 per cent of non-aromatic carbon in alicyclic form.

Test calculations, changing the percentage of hydroxyl, value of B and factor in equation 10 one at a time to the limits just discussed, were made

for coals Nos. 1 and 4 only on the data from infra-red, x-ray, densimetric and refractometric measurements in order to assess the effects on R_a and f_a. Only pericondensed systems were considered since there were few results for catacondensed systems and (see later) they are not likely to be important. The infra-red conversion factor (*Table 3*) of 3 was also the only one considered because values of R_a from the lower values of the factor are much too high in

Table 10. Effect of changing assumptions regarding oxygen groups
(Percentage of oxygen as hydroxyl = 60 ±20%)

Method	*Mean changes (Coal No. 1 → Coal No. 4), %*	
	R_a	f_a
Infra-red	±8 → 0	*V. small*
X-Ray	*Negligible*	±2
Densimetric	±30 → 8	*Nil*
Refractometric	*Nil*	±2

Table 11. Effect of changing value of B
($B = 2 \mp 0{\cdot}5$)

Method	*Mean changes (Coal No. 1 → Coal No. 4), %*	
	R_a	f_a
Infra-red	±20 → 15	*Nil*
X-Ray	±1·5	±2
Densimetric	±45 → 30	*Nil*
Refractometric	*Nil*	±1½ → 1¼

Table 12. Effect of changing factor in equation 10
(Factor = 1·875 ± 0·075)

Method	*Mean changes (Coal No. 1 → Coal No. 4), %*	
	R_a	f_a
Infra-red	±20 → 10	*Nil*
X-Ray	±1 → 0	±1½ → 1
Densimetric	±15 → 10	*Nil*
Refractometric	*Nil*	±2 → 1

comparison with other estimates. Results of these test calculations were expressed as percentage change in R_a and f_a. It was assumed that the nuclear magnetic resonance results would change roughly to the same extent as those from infra-red data, whereas those from heat of combustion would change as those from x-ray measurements. The parameters derived by the methods of this paper are alone subject to change from these variations; i.e. only R_a is variable in the infra-red, n.m.r. and densimetric methods and (virtually) only f_a in the refractometric method, but both are variable in the x-ray and heat of combustion methods. *Tables 10* to *12* summarize the conclusions.

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A decrease of R_a and f_a is brought about by decrease of hydroxyl, increase in the value of B, and decrease in the factor from equation 10; and vice versa. When there is a clear variation with rank the tabulated values for coals Nos. 1 and 4 are shown separately and joined by an arrow.

The use made of these calculations is discussed in the next section.

COMPARISON OF RESULTS AND APPRAISAL

Where results for catacondensed systems are obtainable they tend to reduce discrepancies between methods, i.e. they bring the estimates of R_a from densimetric and refractometric methods closer to each other and to those from most of the other sources. But since these other estimates refer to pericondensed systems the improvement is illusory. The values for catacondensed systems are only obtainable for some coals in three of the methods and do not alter the values from any of the direct experimental methods. This difference between the cluster shapes is unimportant for the average values of R_a later deduced (*Table 14*), and it may be assumed for the purposes of comparison that the shape of the ring clusters is somewhere near to the pericondensed form. These values alone will be used in the remainder of this paper.

The hydrogen/optical density factor of 1 used in *Table 3* leads to unduly large values of R_a and small values of f_a and also a maximum value of R_a for coal No. 4—clearly it must be rejected. To a lesser extent the factor of 2 leads to similar difficulties but it is considered in the appraisal because it is the average factor chosen by J. K. BROWN in his papers[8,10]. The factor of 3 leads to more reasonable results though the increase in R_a at the highest ranks is less marked than that estimated from other methods.

In *Table 13* estimates of all the main parameters from the six methods considered earlier are collected together. These correspond to the assumptions 60 per cent of total oxygen as hydroxyl, $B = 2$, and factor in equation $10 = 1{\cdot}875$.

Changes in the above assumptions affect results from some methods more than those from others; those most sensitive are the infra-red, n.m.r. and densimetric methods. It is therefore possible, by changing the assumptions, to alter the considerable discrepancies between different methods that are apparent in *Table 13*, and in particular to test whether they are absolute or can be made to disappear. The same changes in assumptions must of course be made for all methods.

The effects on R_a are much greater than those on f_a; this is fortunate because it is desirable to lower the values of R_a from infra-red and n.m.r. methods but to increase the values of f_a, which changes in the assumptions cannot simultaneously do. R_a values from the densimetric method are lower than all others and further decrease is undesirable; but since more doubt attaches to the densimetric method than to the infra-red and n.m.r. methods, the two latter must determine the changes in limits to be adopted. This suggests the use of $B = 2{\cdot}5$ and a value of $1{\cdot}8$ for the other factor. $B = 2{\cdot}5$ is, however, rather high; with it no result at all can be obtained from the densimetric

Table 13. Comparison of results on standard assumptions
($B = 2$, factor = 1·875, 60 per cent of oxygen as hydroxyl; pericondensed systems)

Coal No.	*Method*	*Remarks*	R_a	f_a	C'_{ar}	$2(R_a - 1)/C'_{ar}$
1	*Infra-red*	*H/opt. dens. factor = 2*	8·0	0·725	26·5	0·525
	Infra-red	*= 3*	5·5	0·75	20	0·45
	N.m.r.	*Upper limit*	3·8	0·78	15	0·37
	N.m.r.	*Lower limit*	4·7	0·76	17·5	0·415
	Densimetric	—	2·0	0·83	9	0·195
	X-Ray	—	2·8	0·80	12·5	0·30
	Refractometric	—	6·3	0·745	21·7	0·475
	Heat of combn	—	11·2	0·71	35	0·585
2	*Infra-red*	*H/opt. dens. factor = 2*	10·6	0·73	33·5	0·575
	Infra-red	*= 3*	6·8	0·76	23·5	0·495
	N.m.r.	*Upper limit*	3·2	0·815	13·5	0·335
	N.m.r.	*Lower limit*	4·5	0·79	17	0·41
	Densimetric	—	2·2	0·845	10	0·235
	X-Ray	—	3·2	0·815	13·5	0·335
	Refractometric	—	7·6	0·75	25·1	0·515
	Heat of combn	—	13·0	0·72	39	0·61
3	*Infra-red*	*H/opt. dens. factor = 2*	10·6	0·76	33·5	0·575
	Infra-red	*= 3*	6·7	0·79	23	0·49
	N.m.r.	*Upper limit*	3·5	0·84	14	0·35
	N.m.r.	*Lower limit*	4·3	0·82	16·5	0·40
	Densimetric	—	2·5	0·865	11·5	0·275
	X-Ray	—	3·6	0·835	14·5	0·36
	Refractometric	—	9·2	0·77	29·7	0·55
	Heat of combn	—	15·0	0·74	44·5	0·63
4	*Infra-red*	*H/opt. dens. factor = 2*	10·6	0·805	33·5	0·575
	Infra-red	*= 3*	6·8	0·835	23·5	0·495
	N.m.r.	*Upper limit*	4·3	0·87	16·5	0·40
	N.m.r.	*Lower limit*	5·5	0·855	20	0·45
	Densimetric	—	3·5	0·89	14	0·35
	X-Ray	—	4·0	0·88	15·5	0·38
	Refractometric	—	11·6	0·80	36·5	0·59
	Heat of combn	—	16·0	0·78	46·5	0·64
5	*Infra-red*	*H/opt. dens. factor = 2*	9·9	0·89	32	0·565
	Infra-red	*= 3*	7·0	0·915	24	0·50
	N.m.r.	*Upper limit*	8·0	0·905	26·5	0·525
	N.m.r.	*Lower limit*	9·0	0·895	29	0·545
	Densimetric	—	5·9	0·93	21	0·465
	X-Ray	—	4·7	0·95	17·5	0·415
	Refractometric	—	16·7	0·855	47·1	0·645
	Heat of combn	—	19·5	0·845	54	0·67

method for coal No. 1. It was therefore decided to use, as the extreme limits, $B = 2{\cdot}25$ and 1·8 for the other factor.

Reduction of hydroxyl oxygen to 40 per cent of the total would also reduce R_a from the infra-red and n.m.r. methods, but in these cases the effects are small compared with those due to changes in the other assumptions; and 40 per cent is improbably low. Hence this possibility has been neglected.

Thus the following percentages were subtracted from the results in *Table 13*: from R_a, 30, 26, 22, 18 and 14 per cent for coals Nos. 1 to 5 respectively for infra-red and n.m.r. methods, and 40, 35, 30, 25 and 20 per cent for the densimetric method; from f_a, $2\frac{1}{2}$ per cent (for all coals) for x-ray, densimetric and heat of combustion methods.

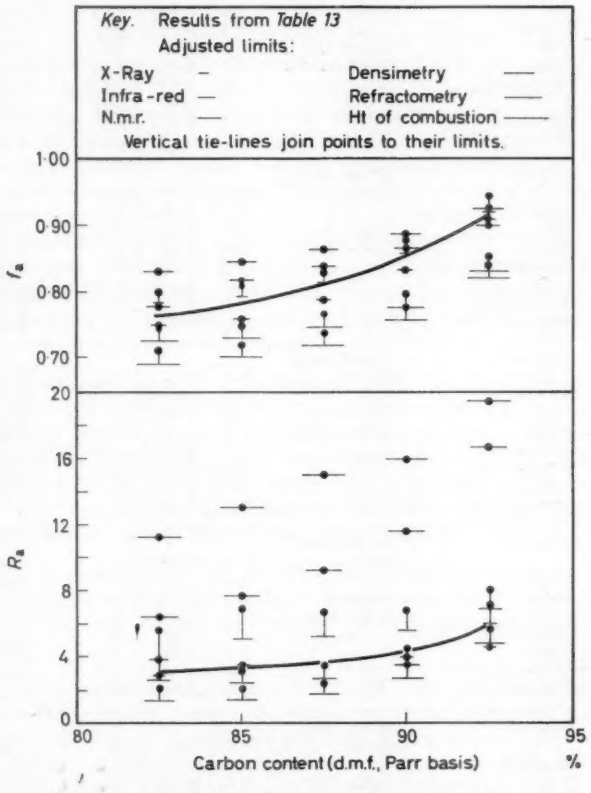

Figure 4. Comparative results

Figure 4 illustrates the variations of R_a and f_a with rank for the six methods, showing both the average values from *Table 13* and the effect of changing the assumptions as just discussed. Infra-red results for a hydrogen/optical density conversion factor of 3 alone have been plotted since this gives the lowest R_a values; similarly, only n.m.r. results for the upper limit (*Table 5*) are shown.

The densimetric values of R_a now appear too low and the corresponding values of f_a too high; conversely for the refractometric and heat of combustion methods R_a values are too high and f_a values too low. In the original

paper on heat of combustion lower values of R_a than those listed here were obtained but the method used to derive them from values of $2(R_a - 1)/C'$ was crude, and the derivation of f_a there used has been shown in the present paper to be invalid. It must be concluded that in deriving the basic values which form the point of departure in this paper, either the densimetric, refractometric* and heat of combustion methods must embody some incorrect assumptions or the selection of reference compounds must be inadequate. This supports an earlier suggestion[2,13], that since the interpretation of x-ray and other measurements has now advanced sufficiently, the future value of statistical structural analysis will lie mainly in the field of assessment, as for example it has been used in the present paper.

It is clear that results from n.m.r. can be made to agree with those from x-ray diffraction; but results from n.m.r. and infra-red spectroscopy cannot be made to agree without further modifying the basic data or assumptions. Values of the optical density ratio are experimentally inaccurate at low rank owing to the close proximity of the strong hydroxyl absorption band and the weakness of the aromatic C—H band: values below 85 per cent carbon content have had to be extrapolated. Errors due to mutual overlap of the two C—H bands measured are also less important at high ranks where they approximate to equality in height; but against this the change in the ratio with carbon content is very rapid at high rank and the values shown in *Table 14*, taken from the smoothed curve, may be appreciably incorrect for this reason. It remains possible that the conversion factor from optical density to hydrogen is greater than 3 for coals, since the number of pure compounds studied was not great and they may not have included the structures most closely similar to that of coal. Alternatively the interpretations and approximations used by Hirsch[9] and by Richards[16] may require further modification.

A more fundamental possibility is that the entire structural model for coal on which these interpretations and the methods of the present paper have been based is incorrect.

One of the initial objects of this paper, namely the selection of the best set of parameters (describing the structural model assumed) available, can now be attempted if the results from infra-red, n.m.r. and x-ray measurements—which are in closest mutual agreement—are alone taken into account. These moreover fall within the limits of those from the other methods.

Mean values of R_a and f_a between the three sets mentioned have therefore been taken for each coal and smoothed curves drawn. To ensure self-consistency, values of $2(R_a - 1)/C'_{ar}$ corresponding to values of R_a from these curves were read from *Figure 3*, and added to values of H'_{aru}/C'_{ar} calculated from f_a and equation 10. The sum was within 2 per cent of unity for all five coals and values of the two ratios were adjusted proportionately, making the sum exactly equal to unity, to ensure consistency according to equation 2. Adjusted values of R_a and f_a were then calculated from the adjusted ratios;

* The determination and selection of appropriate refractive indices for polycyclic aromatic compounds is difficult, and complicated by their anisotropy. Moreover the presence of non-alternant aromatic structures would enhance the indices to be expected and thus lower the deduced values of R_a.

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curves joining these have been superimposed on *Figure 4*. These final adjusted values, with other corresponding parameters, have been collected in *Table 14*. A column has been added to show the conversion factor for optical density to hydrogen needed if the smoothed infra-red estimates chosen are to agree with these mean results and the type of coal structure assumed. The values of this factor show no steady trend with rank and the average value to secure agreement would need to be 4·0. If, however, bearing in mind the discussion

Table 14. Preferred values of the main parameters, and comparison with infra-red estimates of peak intensities

Coal No.	*% C, d.m.f. (Parr basis)*	f_a	*Atoms and rings per cluster unit*						$\frac{2(R_a - 1)}{C_{ar}}$
			R_a	C'_{ar}	$C'_{al+alic}$	H'_{ar}	$H'_{al+alic}$	H'_{aru}	
1	82·5	0·765	3·1	13·2	4·05	3·8	8·4	8·9	0·325
2	85	0·785	3·3	13·7	3·75	4·4	7·8	9·0	0·34
3	87·5	0·815	3·7	15·0	3·4	5·4	7·05	9·5	0·365
4	90	0·855	4·4	17·0	2·9	6·6	6·0	10·1	0·405
5	92·5	0·92	6·1	21·2	1·85	8·25	3·85	11·2	0·47

Coal No.	*% C, d.m.f. (Parr basis)*	*% of pure coal by wt*			*H ratio*	$\frac{D_{ar}}{D_{al+alic}}$ *(i.r.)*	*Ratio*
		$C_{al+alic}$	$H_{al+alic}$	H_{ar}	*(a)*	*(b)*	*(a)/(b)*
1	82·5	19·4	3·39	1·52	0·45	0·115	3·9
2	85	18·3	3·20	1·80	0·565	0·13	4·35
3	87·5	16·2	2·83	2·17	0·765	0·175	4·4
4	90	13·1	2·28	2·49	1·10	0·27	4·1
5	92·5	7·4	1·30	2·77	2·15	0·635	3·4
					Mean H/opt. dens. factor required		4·0

three paragraphs back, the value of the optical density ratio for coal No. 5 is regarded as the most accurate of the five values but is increased to 0·75, which is well within the scatter of the experimental points, the infra-red results may be brought into agreement with those of *Table 14* even while retaining an extinction coefficient ratio of 3 or less, i.e. one within the range of those for the pure compounds studied by Brown. Such adjustments to the smoothed experimental values taken would incidentally increase the infra-red estimates of R_a more rapidly above 90 per cent carbon, giving closer agreement in rank-trend with other methods and with the average values in *Table 14* (cf. the second paragraph of this section, page 460).

The various assumptions that correspond to the values in *Table 14* must here be recapitulated both for the record and because they themselves may throw some light on coal structure if it resembles the assumed model.

(*a*) Aromatic nuclei are pericondensed (this is not critical and 10 per cent deviation towards catacondensed would make scarcely any difference; moreover with such small numbers of rings the differences between the two shapes are not great).

(*b*) *B* averages 2·25 linkages from any one cluster nucleus to others.

(*c*) The factor in equation 10 should equal 1·8 (not 1·875), implying a high proportion (actually 80 per cent though this is not necessarily true) of non-aromatic carbon in alicyclic form.

(*d*) 60 per cent of the total oxygen is in the form of hydroxyl groups (this is not critical).

(*e*) The upper limit of the n.m.r. results leads to slightly better overall agreement with the averages later selected (*Table 14*), which implies that most of the methyl groups in coal may be in the *peri* position or otherwise in close proximity. This is not unreasonable if one considers the difficulties encountered in assembling a molecule of the type envisaged[3].

To these assumptions must be added the conclusion that the infra-red hydrogen/optical density conversion factor may need to be higher than would be expected (actually 4 or at least 3 instead of 2 as assumed by Brown[10]).

DISCUSSION

Where values for catacondensed systems were unobtainable the physical meaning is as follows: unless the indicated value of f_a exceeds 0·8 (coal No. 1) or 0·95 (coal No. 5), then since the non-aromatic carbon requires a definite allocation of hydrogen, the amount remaining for the aromatic carbon is sufficient only for a pericondensed ring system.

It is important to note that the present analysis has shown the results of Brown as interpreted in his paper[10] to be incompatible with those of Hirsch[9]; this invalidates the combined treatment of the two sets of results attempted in their joint paper[8], even though the x-ray values there used were earlier estimates[20] using which the discrepancy was smaller, and it illustrates the discriminatory value of the tests here developed. It is, however, just possible, within the experimental error, to bridge the gap between them. The results of van Krevelen and Schuyer[5] obtained respectively by densimetric and refractometric methods are also incompatible and should therefore not be used, as has been attempted, in combination to give a complete picture of structure.

In addition to the results used in this paper Hirsch[9] has reported values of the 'fraction of amorphous carbon', with a caution against attaching any precise interpretation to them. Hirsch suggests that aliphatic carbon attached to the ring system will only contribute partly to this amorphous fraction so that the fraction of aliphatic carbon should be higher than the fraction of amorphous carbon. Thus these measurements of Hirsch suggest much higher values of the fraction of aliphatic carbon than those deduced from his layer-size measurements by the method used in this paper. There is a large discrepancy here that should provoke further consideration. There may be a minor possible error in the present interpretation of Hirsch's layer-size measurements if aliphatic bridges consist of a single methylene group. Such a bridge may (in the x-ray pattern) contribute a complete carbon atom to the

ordered structure of each of the clusters it inter-links, instead of only half an atom as it should if a true picture of the structure is to be deduced.

Whether the slight minimum in the value of R_a shown by the results from n.m.r. measurements at 85 to 87·5 per cent carbon is significant must remain doubtful. Though the minimum in this region found by van Krevelen and Schuyer[5] can no longer be discounted for the reasons earlier given[2] by the writer, since estimates of quinone concentrations have increased and ether oxygen therefore appears negligible, it still cannot be supported because the method of derivation was not rigorous and the methods used in this paper disclose no such minimum using the same data.

The average values of R_a in *Table 14* (*Table 1* suggests that they may be low by about 0·5) are not far removed from those suggested by Hirsch in his most recent paper[9] and do not conflict with the somewhat negative conclusion reached some years ago by J. B. NELSON[21] from his own X-ray measurements. They are, however, significantly lower, and values of f_a at low rank significantly higher, than those adopted by van Krevelen and Schuyer in their book[5]. It has already been pointed out that values of the aromaticity f_a are significantly higher than those adopted by Brown and Hirsch[8].

It may be questioned whether a high proportion of alicyclic carbon (point *c*, p 465) would leave sufficient bridge methylene to allow B to have the value 2·25 (point *b*), since for steric reasons the majority of inter-cluster bonds cannot directly link carbon atoms in different nuclei. *Table 14* shows that methylene carbon could amount to nearly one atom per cluster unit (coal No. 1) falling to approximately half an atom (coal No. 5). If all linkages were effected by single methylene groups, $B = 2{\cdot}25$ would require just over one atom per unit, so that the proportion of direct linkages need not be unduly high and assumptions *b* and *c* are not necessarily incompatible. B may well vary slightly with rank.

Finally a study of *Table 14* shows some interesting trends with rank. The ratio H'_{ar}/R_a is little greater than unity, and shows a maximum at 90 per cent carbon (H'_{ar}/C'_{ar} correspondingly is the same for coals Nos. 4 and 5). The low ratio of just over one hydrogen atom per ring suggests why aromatic character is not marked in the chemical reactions of coals, since this character is commonly recognized by reactions in which the hydrogen is replaced by other groups; P. H. GIVEN[22] has already drawn attention to this point. The maximum can be explained by the conflicting trends due to decreasing degree of substitution and increasing number of rings as rank increases. A measure of substitution is given by the percentage difference between H'_{aru} and H'_{ar}; this falls steadily, with rank increase, from 60 per cent to 25 per cent, a finding consistent with the qualitative conclusion deduced by Brown[10] from the character of the infra-red spectra in the range 700 to 900 cm^{-1}.

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GLOSSARY OF SYMBOLS USED

Symbol		
C	total carbon content	Percentage of pure coal (d.m.f., Parr basis)
C_{ar}	aromatic carbon content	
$C_{al+alic}$	non-aromatic carbon content	
H	total hydrogen content	
H_{ar}	aromatic hydrogen content	
$H_{al+alic}$	non-aromatic hydrogen content	
H_{aru}	aromatic hydrogen content in unsubstituted cluster equivalent to actual average cluster	
H_{OH}	hydroxyl hydrogen content	
H_0	$H_{ar} + H_{al+alic} = H - 0{\cdot}0375\,O$	
H_1	hydrogen in hydrocarbon equivalent of coal molecule, $= H + 0{\cdot}025\,O$	
O	total oxygen content	
All above with dash (e.g. C')	same expressed as atoms	Per cluster unit
R	average number of fused aromatic and alicyclic rings	
R_a	average number of fused aromatic (6-carbon) rings	
B	average number of linkages*† leading from any one cluster unit to others $= 2l/(m-1)/m$	
B_0	average number of linkages‡ leading from any one cluster unit to others directly between aromatic nuclei	
	* including aliphatic bridges. † linkages via oxygen can only be a small proportion of the total and are allowed for in the 'oxygen correction' to hydrogen. ‡ excluding aliphatic bridges.	
C'_0	number of ordered atoms per lamina, from X-ray measurements	Miscellaneous
f_a	(x in the writer's previous papers) fraction of total carbon in aromatic combination	
f	fraction of total carbon in aliphatic combination	
k	ratio of non-aromatic hydrogen atoms to non-aromatic carbon atoms	
l	number of linkages joining the more central cluster units in the molecule to others	
m	average number of cluster units per molecule	
n	average number of carbon atoms in aliphatic chains in coal	
r_0	ratio approximating to $H_{ar}/H_{al+alic}$ (determined by n.m.r. method)	
r	r_0 corrected for hydrogen as hydroxyl	
$2(R_a - 1)/C'_{ar}$	van Krevelen's 'ring condensation index' applied to the aromatic rings only; related to number of fused rings, zero for benzene and unity for graphite.	

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Recent Developments and Notes

DR RUDOLPH LESSING, C.B.E.

The appointment of Dr RUDOLPH LESSING in the Birthday Honours in June as Commander of the Order of the British Empire is very gratifying to his many friends working in the field of fuel technology. It is particularly appropriate at the present time when the regulations of the Clean Air Act are being put into effect. The work of Dr Lessing in connection with smoke abatement over a long period is well known and at the present time he is the president of the National Society for Clean Air.

Of all Dr Lessing's contributions to fuel technology one of the most important is that of being one of those mainly responsible for the publication of *Fuel in Science and Practice*, the name under which the present journal *Fuel* was first issued in January 1922. This arose out of a decision of the Coal Research Club, of which he was a joint founder with the late R. V. WHEELER in 1921, to issue a journal devoted to the science of fuels and their utilization. This was the first journal in English to deal exclusively with this particular branch of technology and is still the only one providing a forum exclusively for original papers in fuel science. The association of Dr Lessing with the journal has continued throughout its existence. First, he was Review Editor, then Joint Editor and later Editor, from 1940 to 1947. From 1948 he has been a member of the Editorial Committee of *Fuel*.

FRENCH AWARD
TO DR D. T. A. TOWNEND

Dr D. T. A. TOWNEND, C.B.E., Past President and Melchett Medallist of the Institute of Fuel is to be one of the first recipients of the award of the Gold Medal of the Institut Français des Combustibles et de l'Energie. This is a new foundation of the French Institute, designed to recognize outstanding scientific achievement in the field of utilization of fuel and power. As the first eminent British fuel technologist to be so honoured, he will receive the award at a ceremony in Paris in the autumn.

Dr Townend's career began in collaboration with the late Dr W. A. BONE, then Professor of Chemical Technology at the Imperial College of Science and Technology, and with Dr D. M. NEWITT, now Courtaulds Professor of Chemical Engineering and Pro-Rector of the college. He became successively Salter's Research Fellow, Rockefeller International Research Fellow, and Hon. Lecturer at the College before being appointed in 1938 Livesey Professor of Coal Gas and Fuel Industries at Leeds, where he remained with increasing activities in the University and for various Ministries until 1945. Dr Townend was then appointed Director-General of the British Coal Utilisation Research Association.

His early work, particularly that on combustion at high pressures and on the mechanism of 'cool flames', amongst other problems, has resulted in substantial contributions to the scientific literature on fuel technology. His

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work in administration of research and development has further advanced knowledge and practice in fuel utilization.

RESERVES OF SOLID FUELS

At the instigation of l'Institut National de l'Industrie Charbonnière (INICHAR) P. LARDINOIS has made an important comprehensive and critical study of the published estimates of world reserves of solid fuels [*Ann. Min. Belg.* (1958) 93 to 153]. He has examined the basis of these estimates which is not by any means always clearly defined. As far as possible the most probable values have been chosen and reduced to a uniform basis in order to calculate how far the available reserves of coal and lignite will satisfy the demands for energy which are predicted for the future. The author proposes that classes of reserves should be specified, such as certain, measured or proved reserves, probable reserves, possible reserves, uncertain reserves, total reserves (the sum of the first three classes), original reserves, and recoverable fuel, that is, the effective recoverable reserves taking into account all losses. He also takes into account the thickness and depth of coal seams.

After taking these factors into account, together with the conversion of the values for reserves to a basis of calorific equivalence, the author proposes that a *coefficient of reduction* should be applied, say 0·8 for certain, 0·6 for probable and 0·5 for possible reserves. A table of minimum reserves arrived at by this treatment is given, as well as one of minimum and maximum reserves according to earlier estimates. A bibliography of 146 references is appended.

NORTHERNMOST OIL REFINERY

Neste Oy, Finland's first petroleum refinery, at Naantali, near the south-western port of Turku, has come on stream in the past few months and is operating at 115 per cent of capacity. It is controlled by the Finnish Government and its output will meet about half of Finland's requirements for petroleum products. The refinery was designed and engineered by The Lummus Company of New York and its European subsidiaries in Paris and The Hague.

The refinery includes an electrical desalting unit, atmospheric and vacuum distillation unit, catalytic reforming, cracking and polymerization units. It is claimed that Neste Oy is the first complete refinery in Europe to have a fully electronic instrument control system [*Inst. Petrol. Rev.* 12 (1958) 84].

BUREAU OF MINES INVESTIGATIONS OF COAL

Publications concerning U.S. Bureau of Mines investigations of coal and its products from 1910, when the Bureau was established, to 1935, are listed in *Tech. Pap. U.S. Bur. Min. No. 576*, publications from 1935 to 1940, in *Tech. Pap. No. 639*, those from 1940 to 1945 in *Tech. Pap. No. 698*, and those from 1945 to 1950 in *Bull. U.S. Bur. Min. No. 528*. A recent publication, *Inform. Circ. U.S. Bur. Min. No. 7825*, covers the publications from 1950 to 1955.

OXIDATION OF DIESEL OIL

A paper by S. R. SERGIENKO, P. N. GALICH and V. I. TEVLEV gives an account of an investigation of the effect of aromatic hydrocarbons on the character of the oxidation of hydrocarbon mixtures [*Zh. prikl. Khim.* (*J. appl. Chem., Moscow*) 29 (1956) 1716]. The *iso*paraffin–*cyclo*paraffin portion of diesel fuel was separated by adsorption chromatography and to this portion were added varying amounts of di*iso*propyl benzene to study the effect of aromatic hydrocarbons on the oxidizability of the diesel fuel. The initial stage in the oxidation process was found to be the formation of peroxides. This passes through a maximum in the first two hours of oxidation, after which there is a continuous decline in the concentration of peroxides in the products. The addition of 10 per cent of di*iso*propyl benzene has no appreciable effect on oxidation, but 25 per cent or more inhibits oxidation and may go so far as to stop it completely. Oxidation does not appear to be inhibited by the di*iso*propyl benzene, but by the decomposition products of its peroxides. The most stable diesel fuel is that containing 20 to 25 per cent of aromatics.

PETROGRAPHIC STUDY OF COAL

B. IONESCU-SISESTI has described results of a petrographic study of coals which are at variance with the generally accepted views on the petrographic constitution of coal [*Stud. Cercat. Energ.* 7 (1957) 73; abstract in *Chem. Abstr.* 52 (1958) 1585, 1586]. The author considers that vitrain, clarain, durain and fusain are only extreme varieties of a number of individual species. In the vitrain series there is a constituent designated as fusitized vitrain, which has not previously been identified. Another new material, called colofusain, was identified in the fusain series. It appears to be similar to fusitized vitrain and the author suggests that this challenges the usually accepted theory that vitrain and fusain were formed by different processes. Durain is considered to be only a member of a duritic agglomerate, or clarain-type series, formed by segregation during the peat formation process. The existence of a mineralized vitrain is also mentioned.

NATIONAL CHEMICAL LABORATORY

The Lord President of the Council has approved changes in the functions of the Chemical Research Laboratory, Teddington, Middlesex, by the Council for Scientific and Industrial Research. In addition the name of the Laboratory will be changed to the National Chemical Laboratory.

The Laboratory will concentrate its effort on a few objectives, covering only a limited part of the whole field of chemical research, so as to be able to make a real impact on selected problems of national importance such as: the determination of the fundamental physicochemical properties of chemical compounds which are required, for example, by chemical engineers for the design of full-scale industrial plant; the related study of the development of techniques of purification of materials such as metals and chemicals, with a view to the supply of standard samples of pure substances for reference purposes; fundamental and applied studies of the corrosion of metals; the extraction of elements of atomic energy interest from low grade ores.

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SHELL GASIFICATION PROCESS FOR SOUTH EASTERN GAS BOARD

A licence has been granted to the South Eastern Gas Board by N.V. De Bataafshe Petroleum Maatschappij (associates of the Shell Petroleum Co. Ltd) for the use of the process developed by them for the production of crude synthesis gas from a range of oil feedstocks. This process, known as the 'Shell Gasification Process', employs a gasification system with oxygen under pressure.

The South Eastern Gas Board have placed a contract with the Woodall-Duckham Construction Co. Ltd for the erection of the first plant using the new process for the production of town gas. It will be built at the Board's new works adjoining the B.P. Refinery at the Isle of Grain and will be the second stage of development on the site, the first stage of which is nearly completed.

The plant will cost about £3 000 000 and will produce 20 000 000 cubic feet a day. The gas, when processed, will have a very low sulphur content; it will contain so little carbon monoxide that the risk of gas poisoning will be almost eliminated.

INDUSTRIAL POLLUTION OF AIR AND WATER

Two conferences, each for two days, were held in London in September and December 1957, organized by the Iron and Steel Engineers Group of The the Iron and Steel Institute to consider 'Air and Water Pollution in the Iron and Steel Industry'. Twenty five papers were presented by authors from Austria, France, Germany, the U.S.A. and the U.K. and there were present representatives from several other countries. The proceedings of the conferences have now been published [*Spec. Rep. Iron St. Inst., Lond., No. 61* (1958) 260 pp]. The following observations may be noted for their interest and importance.

The increased extent of iron-ore preparation and sintering has created new problems. Also the use of liquid fuels and harder driving has resulted in more oxide-fume emission from open-hearth furnaces, particularly when oxygen lancing is also employed.

A grid survey of an area such as that at Port Talbot, South Wales, in respect of emission of grit and sulphur gases is essential for obtaining a correct picture. Whilst there are considerable points of resemblance between the dust and sulphur trioxide contours in the above area, the two are not by any means identical. The differences are mainly traceable to known causes.

The capital cost of plant for cleaning waste gas is rarely the prime factor in choosing a plant, for running costs must be taken into account and an appreciable proportion of these costs can only be assessed from practical experience.

The major problems of air pollution in sinter plants are considered to be overcome and the future will show very marked improvements in the control of dust at these plants.

The Collin process for the desulphurization of coke-oven gas is operated with success on the coking plant of Stewarts and Lloyds Ltd at Corby, sulphur removal being to the extent of 70 to 75 per cent and the quantity of acid produced is just about sufficient to meet the requirement for ammonium-sulphate manufacture in the by-product plant.

A pilot plant developed by Institut de Recherches de la Sidérurgie (IRSID) for the removal of iron-oxide dust from the red fumes arising in the pre-refining of iron oxide, is able in industrial use to precipitate more than 99 per cent of the oxide particles.

As distinct from existing processes of flue-gas washing, the Fulham–Simon-Carves process has the outstanding advantage of producing saleable products to offset the cost of operation. A pilot plant is now operating this process on half-boiler scale at the North Wilford generating station, Nottingham.

The process of biological treatment of coke-oven effluents has been established as an economic proposition, especially in comparison with chemical methods of treatment. The degree of purification, as measured by the permanganate value, is not less than 90 per cent. Many problems, however, remain to be solved, especially in the microbiological and chemical fields.

INDIAN SYMPOSIUM ON THE NATURE OF COAL

A symposium on 'The Nature of Coal' is to be held at the Central Fuel Research Institute, India, from 9 to 11 February 1959. It is being organized by the Central Fuel Research Institute, the Institute of Fuel (India Branch) and the Institute of Chemists. There are to be six sessions: (*i*) origin and systematics of coal, (*ii*) petrographical x-ray studies of coal, (*iii*) ultrafine structure of coal, (*iv*) coal constitution: physical methods, (*v*) coal constitution: chemical methods, (*vi*) physicochemical properties of coal.

Papers to be presented at the symposium should not exceed 3000 words and should be sent, with their abstracts, to reach The Director, Central Fuel Research Institute, P.O. Fuel Research Institute, Dhanbad Dist., Bihar, India, not later than 31 October 1958.

NUCLEAR FUEL CYCLES

A symposium is to be held in London on 'Nuclear Fuel Cycles' on 22 and 23 January 1959, arranged by The Institute of Physics, which is one of the constituent bodies of the British Nuclear Energy Conference.

There will be three sessions dealing with: (*i*) (*a*) long-term reactivity changes, (*b*) theory of once-through fuel cycles, (*c*) perturbations due to fuel cycles, (*ii*) optimization of fuel cycles for nuclear power stations, (*iii*) fuel cycle operational problems.

The papers to be presented will deal with the applied physics aspects of the fuel cycles which form the basis of the immediate nuclear power programme. Abstracts, but not preprints, of the papers will be available early in January.

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Application forms for tickets to attend the symposium are obtainable from the Secretary, The Institute of Physics, 47 Belgrave Square, London, S.W.1, and should be returned as soon as possible.

NUCLEAR POWER STATIONS

The need for making the fullest possible use of the electricity to be generated in nuclear power stations, even by three-shift working in industry, and the necessity of bringing down the cost of nuclear power plants were emphasized by Sir CHRISTOPHER HINTON, F.R.S., Chairman of the Central Electricity Generating Board when speaking on the development of nuclear energy for electricity supply in Great Britain, at the British Electrical Power Convention held at Brighton in June. He said the alternative was either to swing back to the use of conventional power stations or to produce electricity more expensively than it could be produced in conventional plants.

He recalled that the United Kingdom's programme for the industrial use of nuclear power, published as a White Paper in 1955, envisaged the construction by 1965 of nuclear power plants having a total capacity of between 1 500 and 2 000 megawatts. In fact the target which was aimed at was 1 800 megawatts, equivalent to about 5 million tons of coal a year. The cost of power from these nuclear power plants was estimated to be about 0·6*d* per unit and this was stated to be approximately equal to the cost of producing electricity in the conventional power plants which were then being designed.

During the summer of 1956 there was considerable development of thought which led to a very great expansion of the programme and in March, 1957, it was announced that the programme would be expanded, and the target for 1965 would be lifted from its initial level of 1 500 to 2 000 megawatts to a level of 5 000 to 6 000 megawatts.

The large expansion of the programme which was adopted in 1957 brought with it a major problem. The cost of electricity produced in nuclear power stations had been based on the assumption that these power stations would work as base load stations with an annual load factor of 75 per cent. To use nuclear power stations in such a way was obviously wise because of their high capital cost, but it was a privilege which they could not enjoy indefinitely unless system load factors were considerably increased, by, for example, three-shift working in industry. At present the load factor on the British electricity supply system was under 50 per cent and the minimum continuous load was only about 3 000 megawatts. This occurred at night during week-ends in the summer and was, in effect, the base load on the system.

At the same convention Sir CLAUDE GIBB, F.R.S., Chairman and Managing Director of Messrs C. A. Parsons & Co. Ltd, in presenting a paper on the development of nuclear energy for electricity supply overseas said that the case for a major programme of nuclear power stations was for Britain essentially one of urgent need. With some other nations the production of electricity from nuclear fuel could only be justified on the basis of national prestige or else as a by-product of a military programme. The driving force in Britain being need, it had inevitably led to a somewhat different approach from that which might have been taken had it been a case of prestige or normal industrial development in a new field of engineering. In the latter

case, more time could have been taken in research and development study of more alternative types of reactor before becoming committed to a large-scale programme of construction costing hundreds of millions of pounds.

It was difficult to conceive that Russia for instance, with its huge hydro-electric resources, its vast coalfields, and with all human rights subordinated to the needs or demands of the State, could justify on technical or economic grounds the construction of nuclear power stations on the scale of Britain, yet in order to secure leadership in the peaceful nuclear field we may expect shortly to hear of Russian achievements in the generation of power by nuclear methods. One would expect their programme to be based upon the use of an enriched fuel, so as to keep diffusion plants in continuous operation and ready for military production at short notice. In this event it might well become Russian policy to provide enriched fuel on loan or at absurdly low prices for reactors of Russian manufacture, not only to satellite countries but to less developed nations not yet tied to or allied with Russia but who automatically would become so by acceptance of Russian fuel and nuclear techniques as the basis for their power programme.

COAL RESEARCH IN ALBERTA

In the report for 1957 of the Research Council of Alberta which has recently been issued [*Rep. Res. Coun. Alberta No. 77* (1957)] reference is made to work that has been done in an attempt to set up standard procedures which can conveniently be used to determine volatile matter in sub-bituminous coals and lignites. In the coal laboratory of the Research Council it has been found that the modified British Standard method does not give consistent results on these coals, and that the French double-crucible method, while apparently accurate, is somewhat slow and cumbersome. It has been suggested by several investigators that a single-crucible method with a heating schedule approximating to that of the French double-crucible method should be developed.

Differential thermal analysis studies, that have been made to explore the course of coal pyrolysis, have been extended to cover the effect of different heating rates and of various reaction *modifiers*, and the thermograms of several coal fractions and of three dated fossil woods were determined. The results agree with those of some previous work and it is concluded that the concept of coals as a series of clathrate compounds derived from cellulose and lignin merits closer attention.

An interesting aspect of the differential thermal analysis work is the observation that sulphur dioxide can cause extensive modification of the course of coal pyrolysis. The initial decomposition stage, between 200° and 280°C, appeared to be rendered much more highly exothermic, while there was a marked suppression of the high-temperature decomposition step near 400°C.

RUSSIAN WORK ON THE FISCHER–TROPSCH REACTION

The latest available summary of work done in Russia on the Fischer–Tropsch reaction is contained in a paper by Y. T. Eidus, of the U.S.S.R.

[*Uspekhi Khimii* (*Adv. Chem., Moscow*) 20 (1951) 54], and a translation of this by P. LEVINSON has recently been published by the U.S. Bureau of Mines [*Inform. Circ. No. 7821* (1958)]. The translation was prepared originally for use in connection with the research in the Bureau on the conversion of coal to fluid fuels. Although this paper was published seven years ago it has been made available in English now because of its importance to workers in this field as it is written by an expert and incorporates the results of a great deal of his and other Russian work up to that time. In the bibliography of ninety items there are twenty five Russian papers whose conclusions are considered in the text.

It is stated that Y. T. EIDUS and N. D. ZELINSKII firmly established about 1942 that carbide is not an intermediate in the synthesis of hydrocarbons from carbon monoxide and hydrogen with cobalt or nickel.

Reference is made to catalytic hydrocondensation of carbon monoxide with olefins, as well as the hydropolymerization of olefins under the influence of carbon monoxide, discovered by Eidus and his co-workers, which are very similar to the polymerization of methylene radicals in the presence of hydrogen which is the most important stage in the synthesis after methylene radicals are formed. It is concluded that methylene polymerization, starting with the combination of two CH_2 groups to form adsorbed ethylene, is a continuous combination of CH_2 groups with the simplest olefin molecules adsorbed by dual attachment at adjacent atoms on the catalytic surface.

RESEARCH FOR INDUSTRY

A summary of the work done during 1956–57 by the industrial cooperative research associations grant-aided by the Department of Scientific and Industrial Research has recently been published under the title *Research for Industry 1956–57* (Her Majesty's Stationery Office: London, 1958). Previously this summary of work has been included in the *Annual Report* of the Department of Scientific and Industrial Research, but in future it will be published separately for each calendar year.

In the report of the work carried out by the British Coke Research Association reference is made to an investigation of the factors which influence the bulk density of coal for carbonization. This has been completed and a report has been published but work is now being extended to cover the effect of changes in bulk density on the quality of coke. The bulk density of the coals is determined by a method which has been standardized at Pontypridd and differs from other methods previously given in the literature. Work so far has shown that the Pontypridd method gives more reproducible results than those obtained by the other methods. An attempt has been made to solve the problem of the end-point of carbonization, the method adopted being based on changes in the electrical resistance of coal charges during heating. This involves the design of an electrode accurate enough to give precise results but comparatively cheap and robust for use in large-scale commercial ovens. Work on this subject is promising and will continue.

In the British Coal Utilisation Research Association a modified chain-grate stoker is being developed for Lancashire or Economic boilers, to enable

high efficiency at varying loads to be obtained. Means for directing the air supply preferentially through the thick fuel bed at the front of the stoker have also been introduced and, in certain industrial installations, have been found to enable a high carbon dioxide content in the flue gases to be maintained over a wide range of load. An inexpensive automatic control for the fuel/air ratio in a shell boiler is under investigation, based on the rate of cooling of bimetallic strips by the entering primary air.

Work aimed at improving the ability of the locomotive boiler to use inferior coal is being supported in the Association by the British Transport Commission, which is also running tests under its own auspices to confirm the research findings under service conditions. A new design of ashpan has been developed and is undergoing tests on the railroad.

The Venturi pneumatic pyrometer has been developed for the measurement of gas temperatures in industry. Field tests carried out in the down-takes from open-hearth and glass-making furnaces, and in the open-hearth furnace itself, have shown that this pyrometer gives reliable measurements up to and over 2000°C (3630°F) and responds rapidly to temperature changes. It is less subject to blockage in dusty gases than the suction pyrometer. A more reliable picture of temperature variations with time in industrial processes can thus be obtained with the Venturi pyrometer than by previous methods.

The Motor Industry Research Association is paying attention to atmospheric pollution by engine exhaust gases, especially that caused by diesel-engine exhausts which are often accompanied by dense smoke. Accordingly an advisory panel has been formed to study this question and to make recommendations to appropriate committees of the Association. This panel consists of representatives of vehicle manufacturers, engine builders, oil companies, and passenger transport operators. The initial work which is proceeding concerns the study of a proposed standard apparatus for measurement of smoke emission.

The investigation of the chemical structure and physical properties of tars and tar products, especially new types, has continued in the Coal Tar Research Association laboratories at Gomersal, near Leeds. A much greater proportion of time than formerly has been devoted to the study of present processes since it offers the best possibility of providing immediate financial return to members of the Association without the expenditure on their part of large amounts of capital. Particular attention has been paid to the extraction of tar acids and the recovery of naphthalene. The development of three new coal tar processes has continued during the year.

DETERMINATION OF HYDROGEN IN MINE AIR

An important development in the use of gas chromatography for the determination of hydrogen in mine air has been made in the Central Laboratory, Manchester, North Western Division, National Coal Board. A laboratory instrument using this technique has been designed to carry out such determinations with a rapidity, sensitivity, accuracy and specificity unattainable in the usual volumetric methods. A 10 ml sample of air is taken for each determination, the separation of hydrogen from the other components of the sample

being effected by adsorption chromatography on a 7 ft column of activated carbon. Nitrogen or argon is used as the carrier gas. Hydrogen is eluted from the column after 40 seconds, other more strongly adsorbed components such as oxygen, methane and carbon dioxide being retained for longer periods. Due to the high thermal conductivity of hydrogen as compared with that of a carrier gas such as nitrogen, it is possible to employ a thermal conductivity cell, with a platinum wire katharometer and d.c. bridge circuit used as the detector. Two ranges, 0 to 1 and 0 to 10 per cent are provided, the output from the bridge circuit being taken via a potential divider to a recording potentiometer of 1 mV span and 1 sec response time, or to a galvanometer of 4 μA full scale deflection, which may be calibrated directly in percentages of hydrogen in the sample. Hydrogen can be determined with a precision of ± 0·005 per cent in samples containing about 1 per cent, and amounts down to 50 p.p.m. can be detected.

METHODS OF CONTROL OF COKE OVEN HEATING

An account has been given by P. HENSON of some important features of several recent coke oven installations in Belgian steelworks, particularly with regard to modern methods of heating control [*Mines et Métallurgie* (1958) No. 1; *Iron Coal Tr. Rev.* 177 (1958) 255]. An important item in achieving the maximum heat efficiency of a steelworks is the ease of interchange of blast-furnace gas and coke-oven gas as the firing medium for the ovens according to availability. In this connection it is said that a real advance has been made in a battery of 38 coke ovens built by Société Coppée, on behalf of S.A. Carbonization Centrale, at Tertre. This is an integral compound underjet oven embodying underjet distribution not only for rich gas, but also for lean gas and combustion air.

In this battery the piers include 26 flues in hairpin arrangement, and the regenerators are divided into 26 cells of such a form that each pair of twin flues constitutes, with the corresponding regenerator cells, 13 independent gas circuits. The mains for lean gas and air feed the ducts which distribute both of these to the bottom of the regenerator cells. Orifice valves control the flow of air or lean gas in each duct, whilst other orifices in the pipes joining the ducts to the cells apportion the quantities of gases led to each flue. Metal slide valves, integral with the tubes distributing the air or lean gas to the bottom of each cell, can be rotated and the area of the passage for the burnt gases to the duct is varied as desired. The suction in any of the 13 circuits on the same pier can thus be regulated readily and to a fine degree. This system thus makes possible the independence of each circuit as regards the flow of gases and the distribution of pressures. The relatively high resistance which the orifices offer to the flow of gases from the channels to the bottom of the cells and the constant temperature of the gases in all the passages, ensure the regulation of the firing with very great precision.

AUSTRALIAN CARBONIZATION STUDIES

The Coal Research Section of the Commonwealth Scientific and Industrial Research Organization, New South Wales, has been carrying out a detailed

investigation of the changes which occur in the structure of coal on carbonization. A résumé of this work has recently been published in *Coal Research in C.S.I.R.O.* (1958, No. 4) 10.

Two methods of investigation were used. In the first method 40 lb charges of coal were carbonized at 900°C under conditions similar to those of large-scale coke-oven practice. After removing the charge and quenching, complete sections were taken through the bed, from unaltered coal to high-temperature coke, and samples were prepared for petrographic analysis. In the second method only a few grammes were carbonized in the laboratory at temperatures from 350° to 700°C and the products were submitted to petrographic analysis.

The results obtained by both methods indicated four distinct phases in the carbonization process. In the first phase plasticity develops between 360° and 380°C, in the still discrete grains of coal. The second phase begins at about 380°C, lasting up to about 400° to 410°C, and is characterized by the appearance of gas-filled cavities. Any resinous inclusions in the coal constitute centres at which these gas vesicles begin to form, otherwise the vesicles first appear in practically structureless areas of vitrinite. In the third phase, between 410° and 420°C, the vitrinite-rich grains continue to enlarge and coalescence of these grains and those of inert material takes place. At 420°C the coalescence process is complete and the microstructure is indistinguishable from that of high temperature coke. The fourth phase, covering the temperature range of 420° to 1000°C, is characterized by a progressive shrinkage of the coke structure.

Development of the coking process, passing from the outside of the charge to the middle, is described in the following way. No appreciable change occurs in the coal in the pre-plastic zone except that, just before softening, a minor proportion of the coal becomes soluble in certain organic solvents. The cellular structure of the coke is more or less fully developed in the very early stages of plasticity. The zone in which observable changes take place is only about $\frac{1}{4}$ in. wide. The overall width of the plastic zone is about $\frac{1}{2}$ in., the exact value depending on the type of coal. The loss of volatile matter during the plastic stage causes intumescence and vesicle structure, making the resultant material more porous and therefore less dense. Continuing loss of volatile matter during the solidification stage causes the semicoke to shrink and crack into fissures. Properties of the coke, such as its hydrogen content, optical reflectance and electrical conductance, are determined more by the final temperature of carbonizing than by the characteristics of the coal.

Experimental work is being continued to establish the carbonizing conditions required for the production of a good foundry coke.

THE AMERICAN COAL TAR INDUSTRY

The chemical potentialities of coal tar, or at least certain types of tar, are receiving at present much more attention in America than for some time past owing to the competition for finished tar products from petroleum and synthetic sources and from European imports. Moreover, there is a considerable increase in interest in the chemical technology of low-temperature tar because of the newer developments in the field of low-temperature coal carbonization in the U.S.A.

The current trends and developments in the American coal tar industry have recently been reviewed by A. F. WILLIAMS [*Coke & Gas* 20 (1958) 245, 268]. The author served in 1957 as Fuels Liaison Officer with the United Kingdom Scientific Mission in Washington, D.C.

The demand for chemicals from coke-oven tar, such as benzene, phenol, cresols, is expanding rapidly. Coke-oven tar can play only a limited part in helping to meet the increasing demand, as the production of the tar is linked with the economy of the steel industry. Improvements in steel technology, such as the reduction of coke consumption consequent on the use of increasingly large quantities of oxygen in the combustion process and also development in the process of hydrogen reduction of iron ore, will offset the greater availability of tar which might be expected to arise from an expanding economy. The coke-oven benzene industry finds severe competition from the petroleum industry in the quality of its product which is virtually sulphur- and paraffin-free. To meet this competition some of the steel corporations have installed at their coke ovens hydro-refining plants, either alone or in combination with Udex extraction plants.

The requirements for cresylic acid for the next few years are regarded as being likely to be met, assuming imports remain at their present level, from petroleum and coal tar sources if all the coal tar or coal tar oils are processed for tar acids. The principal markets for bases, particularly pyridine and quinoline, derived from tar oils and ammonia liquors, are the sulphur drugs, vitamins, antiseptics and fungicides. It is said that a fourfold increase in demand could be met without difficulty.

An increasing use of coal for the production of electric power is expected in the future and it is regarded as economically unsound not to remove first the tar and realize more than its calorific value. The most convenient method of carbonizing finely divided coal, producing a char suitable for burning in power stations and recovering the tar for further refining, is that of fluidized carbonization. The Pittsburgh Consolidation Co. and the Alabama Power Co. are amongst the foremost organizations in this field. The U.S. Bureau of Mines has been devoting a large proportion of the available effort at one of its research stations, Morgantown, W.Va, to the investigation of fluid bed tar. Some authorities express the opinion that low-temperature tar may have better possibilities as regards the value of its products than high-temperature by-product tar. The Bureau believes that some kind of low-temperature carbonization process, probably the fluidized one, will become increasingly popular in the U.S.A. *The General Properties of Low-Temperature Tar* is the title of a recent publication of the Bureau of Mines, by M. GOMEZ, J. B. GOODMAN and (the late) V. F. PARRY [*Bull. U.S. Bur. Min. No. 569* (1958)]. This report summarizes the more important work done in low-temperature tar chemistry in Europe and the United States of America.

PULVERIZED COAL TRANSPORT THROUGH PIPES

In the Kreisinger Development Laboratory of Combustion Engineering, Inc., investigations have been conducted for the past ten years on problems related to pulverized coal transport. An account of this work has now been

published by R. C. PATTERSON, the director of the Laboratory [*Combustion* (*int. Combust. Engng Corp.*) 30 (1958, No. 1) 47]. The programme of work included the study of the performance of a commercial exhauster handling air only, and the performance of the same exhauster handling a commercial range of mixtures of pulverized coal and air; the determination of piping friction losses in the transport of mixtures of pulverized coal and air; the development of methods or devices for preventing erosion of transport pipes, particularly at bends or restrictions; the development of portable methods or devices for measuring coal and air flow individually in a pipe containing flowing mixtures; the development of methods for preventing drifting in transport pipes as an aid to reduction of system pressure losses and maintenance of balanced flow in parallel piping systems. Considerable empirical information has been obtained which is of direct practical value.

FUEL FLOW TEST HOUSE

A new Fuel Flow Test House, the most extensive of its kind in Europe, was opened on 6 June by the Minister of Supply, the Rt Hon. AUBREY JONES, M.P. The Test House has been set up by Firth Cleveland Instruments Ltd, the recently formed subsidiary of Simmonds Aerocessories Ltd, at Treforest, Cardiff. Firth Cleveland Instruments Ltd is a Ministry of Supply design-approved firm for aircraft flowmeters and tank gauges.

The Fuel Flow Test House, will provide facilities for calibrating and production-testing flowmeters, water separators, valves and other fluid handling equipment. There are facilities to test to Government and other official specifications, available to all manufacturers of equipment concerned with liquid fuel products, both in the United Kingdom and in Western Europe.

There is equipment for handling fluids, including instruments for quality and quantity measurement, filters to remove water and dirt from liquid products, remotely operated valves for pipelines to control or shut-off flow, various types of indicators for remote read-out purposes, with signals to operate print-out equipment, or for telemetering purposes.

The general operation in the Fuel Flow Test House is that the hydrocarbon fuels in the main storage tanks pass through the Pumping Station and are distributed to the Test Rigs. After traversing the Water Separator Test Rig the fuel is pumped back into the storage tanks in a circulatory manner. The Flowmeter Test Rigs each have a local pump and reservoir tank and are self-contained, the fuel being diverted into a weighing tank for test purposes. At the conclusion of tests the fuel may be transferred back into the storage tanks. During tests the fuel can be subjected to a range of temperatures between $-40°$ and $+55°C$.

At the present time particular attention is being given to increasing the diameter of the fuel flowmeters for general use with aircraft fuel and models of 4, 8 and 16 in. diameter are working satisfactorily provided the end conditions of use are known at the design stage. Flowmeters have also been designed for use at temperatures as low as $-200°C$ and as high as $450°C$, the former working with liquid nitrogen and the latter with liquid coolants in atomic energy plant.

The transmitter unit of the flowmeter consists of a tubular housing of non-magnetic material with standard pipe connections. Within the housing is a three- or six-bladed rotor of magnetic stainless steel, and surrounding the outer portion of the unit is a protective bakelite or alloy cover which contains the electrical pick-up coils, permanent magnet and associated pole pieces. A flow of fuel through the unit will cause the rotor to revolve thereby generating a sinusoidal voltage in the stator coils having a frequency directly proportional to the rate of flow. An electronic unit connects the flow transmitter to the rate-of-flow and totalizing-flow indicators, with a density corrector acting as a subsidiary control element in the case of a mass-calibrated flowmeter.

ROGA COKING INDEX

J. HAMAKER, director of l'Institut Technique Central T.N.O., Section Chaleur, Delft, Holland, has recently published a report on the use of the Roga index for determining the coke power of coal [*Chal. et Industr.*, No. 390 (1958) 3]. This is instigated by the *International Classification of Hard Coals by Type* (United Nations: Geneva, August 1956). In this classification the coals are divided according to their volatile matter content into nine *classes* which are then sub-divided into *groups* according to their caking properties, regarded as reflecting the behaviour of a coal when it is heated rapidly, as in combustion processes. The caking properties are expressed alternatively either by their crucible swelling number or their Roga index. The author of this paper questions the existence of a precise relationship between the Roga index and the crucible swelling index, at least for the lower values of Roga index, below 25. He asserts that Professor ROGA did not establish his method for these values. The question at issue is not so much the inexactitude of the method, as that it is used in the *Classification* in a wrong way. The method was devised for comparing Polish coals in respect of their coking properties and not their caking properties which are of importance in the burning of coal. From this point of view he describes a modification of the Roga method and discusses its possibilities.

AUTOMATIC DETERMINATION OF VOLATILE MATTER IN COAL

An automatic unit for the determination of volatile matter in coal, coke and char, has been described by R. P. HENSEL and S. A. JONES, of the Research and Development Division, Pittsburgh Consolidation Coal Co. [*Analyt. Chem.* 30 (1958) 402]. In determining the volatile content of these solid fuels the American Society for Testing Materials designates a 7-minute heating period at 950°C, with modification of the heating rate for certain non-agglomerating materials. Conventional manual control prevents close duplication of heating rates and results are often erratic. The apparatus described in this paper permits close control of the heating, is sufficiently flexible to be adapted to a variety of methods, and there is automatic control of the whole operation.

The apparatus consists of a motor-driven screw drive for lowering the crucible at a uniform rate into the hot zone of the Hoskins–Fieldner furnace. This drive is actuated by a timer that permits an initial heating period at the

top of the furnace prior to the gradual lowering. This preliminary gradual heating period overcomes the difficulty of particles being ejected by the shock heating of the conventional method. After this preliminary heating period, which can be pre-set for any desired time interval, the mechanical drive carries the crucible at a uniform speed from the top of the furnace into the hot zone at 950°C. At the end of the lowering cycle a second timer holds the crucible for a 6-minute period in the hot zone, then actuates the return mechanism and the crucible is automatically carried up and out of the furnace, completing the cycle. The apparatus is designed to serve two volatile furnaces simultaneously.

COMBUSTION AND FLAME

The following *Notes* appeared in the September issue of *Combustion and Flame* and may be of interest to readers of *Fuel:*

Injection and combustion of liquid fuels
The tuyère combustion zone of the blast furnace
Effect of sonic vibrations on heat transfer from flames
Fuel flow and combustion
Paris conference on combustion of fuels
Fire research 1957
Radiant heat exchange in a furnace

OVERSEAS CORRESPONDENTS' NOTES

The Editor is grateful for the following information on matters of present interest relating to the fuel science field. The notes on Italy were kindly supplied by Professor C. Padovani and on New Zealand by Professor J. Ivon Graham.

ITALY

*Development of thermoelectric production**

ITALY'S overall electric energy production in 1951 was about 29 thousand million kWh, of which 91 per cent was generated hydroelectrically and 9 per cent in thermal stations, the latter mostly from geothermal installations. In 1957 total production touched 43 thousand million kWh, of which 75·4 per cent was hydroelectric and 24·6 per cent thermoelectric.

In six years total production rose by 14 thousand million kWh, and of this increase only 6 thousand million kWh were provided by hydroelectric plant, while the thermoelectric generating stations supplied 8 thousand million kWh. The geothermoelectric power plants played little part in this increase, their 1951 production of 1·6 thousand million having reached 1·8 thousand million in 1957; it is taken in the true sense of the term.

This rapid development has sprung from the fact that the steam power plant offers increasing advantage over hydroelectric plant, because the gradual exhaustion of hydraulic resources counsels building the cheapest plant first and at the same time makes this type of plant more and more expensive as time passes; above all, the strides made in steam generating station technology with the adoption of improved cycles, increasingly high steam pressure and temperature and plant with ever larger unit capacities, which progress in metallurgy and mechanical engineering have made possible, have played a dominant part.

Finally, no small importance should be ascribed to the fact that Italy, poor in coal, has discovered quite a considerable quantity of natural gas in the Po valley, and has recently succeeded in organizing economical mechanized mining of big lignite seams. The future holds out rosy prospects, for further quantities of lignite, which it seems can be economically mined, have been identified, and sources of domestic petroleum have increased, while greater quantities of distillation residues are available from the higher production now turned out by Italian crude oil refineries.

An economical comparison between hydroelectric and thermoelectric production, with liquid fuels, in Italy, based on the purely theoretical assumption of a continuous level, i.e. basic power, gives the following picture: the capital required to accomplish a theoretical production of this kind with hydroelectric plant only is about five times that required with thermoelectric plant. Since in basic thermoelectric power production fuel accounts for

* The term thermoelectric power is used here for all plant converting calorific power into electric power, including geothermoelectric power plants operating on heat from natural steam like the Lardarello generating station, power stations where heat is generated by burning gaseous, liquid or solid fuel whether domestic or imported, and power plants using heat generated by nuclear reactors.

about two thirds of the cost price, the end figure in this particular case is an overall cost of 3 for thermoelectric production against 5 for hydroelectric; this, of course, is a rough comparison. If the power required were not steady but intended to integrate other power and the maximum plant capacity were not utilized to the full, power from a hydroelectric reservoir generating plant might, in some cases, prove cheaper than thermal power.

Everything points to future power requirements in Italy being covered increasingly by thermoelectric production, whether using the conventional fuels or, later, nuclear fuels, rather than by hydroelectric power.

This will not hold true for world production, where power from thermoelectric plant is currently far the greater, being 70 per cent of the total, while on the other hand immense water resources are available for profitable use in producing cheap electric power.

Italian industry has now put into service the new generating plants which, aided by credit facilities under the ERP programme, it commenced building between 1949 and 1950. Before this the overall capacity of all Italy's thermoelectric power plant was little more than one million installed kW, of which 80 per cent was from 28 plants with a capacity of more than 10 MW and the remainder spread over small power stations mostly installed in industrial establishments. This machinery was mainly used as stand-by and integration plant: in fact the mean utilization in 1951 was only 1 000 hours of operation. Now (in 1957), a full 80 per cent of the total production of 8·7 thousand million kWh, or about 7 thousand million, was generated in 22 large up-to-date power plants with a unit capacity of not less than 25 MW, and of which the eight most recently installed each have a capacity of more than 100 MW.

The mean specific consumption of all these 22 power plants has been of the order of 2 950 calories per kWh, equivalent, that is, to about 300 g of fuel oil per kWh. If due account is taken of the fact that the remaining 20 per cent of the production came from generating plant with a high specific consumption, and of the condenser type, but also a considerable extent in recovery cycle power plants with low specific consumption, the total Italian production can be said to have entailed a consumption of not much more than 3 000 calories per kWh.

It is natural that Italy, the latest arrival in this field, has been able to develop a system of up-to-date power plants and thus achieve a specific consumption below that of other nations who have to derive the bulk of production from older power plants: it is, nevertheless, significant that the specific consumption achieved in Italy is below that of other European countries, and of interest to make comparisons with the most important of these.

In England, where power is produced largely from steam generating stations, the last report of the Central Electricity Generating Board gives an annual production of 67 thousand million kWh with a specific consumption of the order of 3 500 calories per kWh; if to this production from the nationalized power supply system is added the conspicuous quantity of power produced by self-equipped concerns, the total comes to 90 thousand

million kWh, with a mean consumption 20 per cent higher than that of the Italian power plants. Had the British power production been accomplished with the same efficiency achieved here, the coal saved would have been about 100 to 120 g per kWh, or from 9 to 10 million tons.

In France, also a country with up-to-date thermoelectric power plants, production in 1957 touched 32·6 thousand million kWh, of which 14 was produced by the Electricité de France and 18 by self-equipped concerns (iron and steel plants, collieries, railways). The mean consumption at the E. de F. was 3 310 calories per kWh; by and large it may be assumed that overall production, including that from self-equipped concerns, called for 3 400 calories per kWh. In this case, had specific consumption been equal to the Italian value, a full 4 thousand million kWh more could have been produced with the same fuel consumption.

A consumption of 3 000 calories per kWh is equivalent to a calorific-to-electric power conversion efficiency of the order of 29 per cent. If this average result is worthy of mention, equally and even more so is the fact that some of the power plants designed on more modern lines than others, already operating in Italy, have broken outstanding records. For instance, the two power stations at Tavazzano (Milan) and Piacenza may be mentioned. The former, the first designed by Italian engineers, was put into service in 1952, and has a mean specific consumption of 2 340 calories per kWh equivalent to about 37 per cent efficiency. In its first five years operation it has produced a total of more than 4 thousand million kWh, and last year generated 918 million kWh, equivalent to 7 300 hours per annum use of the installed capacity. This power plant, like that at Piacenza which went into service some time later, employs an intermediate superheating and regeneration cycle, at a pressure of 135 atm and a temperature of 435°C, both in the primary and the superheated steam. Both the specific consumption and the utilization factor of these two power plants have set up a real European record which still holds good five years after their initiation.

The pressures, temperatures and cycle chosen for Tavazzano and Piacenza have been used for all the big power plants currently in an advanced stage of construction including Santa Barbara with 270 MW capacity which can produce 1·5 thousand million kWh per annum. It utilizes a lignite field in the Arno valley, assessed at 50 million tons. Mechanized excavation, without tunnelling, will make it possible to use this seam, which lies on an average about 60 m below the surface, to feed the generating station for more than 25 years with a lignite of excellent quality.

Another initiative of the same kind is the 'Città di Roma' power plant, which will use the Trasimeno lignite bed. This station will shortly be put into service, equipped with two 35 MW sets, and will produce about 500 million kWh per annum. An outstanding feature of this plant is that for the first time in a high capacity unit use has been made of forced draught condensers because despite the fact that Lake Trasimeno lies nearby, there was not enough water for the condensation process.

Of plants under construction, the following are of particular importance: the Tifeo power plant in Sicily built for Società Generale Elettrica della

Sicilia with a capacity of more than 200 MW, and turboalternator sets entirely built in Italy; the Bari power plant belonging to the Società Meridionale di Elettricità, with a capacity of 210 MW; the Porto Corsini (Ravenna) station belonging to the Società Adriatica Elettrica with two 70 MW units; the Porto Marghera (Venice) plant belonging to the Vetrocoke company, with two 30 MW sets—all the machinery in these power plants was built by Italian industries. In all these power plants the intermediate superheated cycle, with high pressures and temperatures, has been adopted, so that the specific consumption will be similar to that at Piacenza and Tavazzano I.

Units of even greater capacity are now being installed: one with a unit capacity of 150 MW, built by the Ansaldo company, is at present being assembled at the Civitavecchia power plant belonging to the Società Termoelettrica Tirrena; a unit of the same capacity, likewise built by Ansaldo, at the Chivasso (Turin) power plant belonging to S.I.P.; a 140 MW unit, built by the Società Tosi, at the Società Edison's Genoa power plant.

These units will operate at a steam pressure of about 150 kg/cm² and a temperature of 530° to 550°C, with an intermediate superheating and regenerating cycle, and will have a specific consumption around 2 250 cal/kWh.

A 140 MW unit is also now being installed in a second power plant under construction at Tavazzano. This unit will operate at an even higher pressure (180 kg/cm²) and a temperature of 530°C, with intermediate superheating, and will have a consumption of around 2 200 cal/kWh.

Plans are now being put into effect for the construction of a big power plant by the Società Edison; this should be located in a port on the Tyrrhenian sea and be equipped with units of about 300 MW, which will be the greatest unit capacity in any European power plant: the consumption will be less than 2 100 cal/kWh.

The Azienda Elettrica Municipale (Milan Electricity Board) is also planning to build a power plant near Milan.

Of the power plants with part or total recovery which are in an advanced stage of construction—that is, plants where the exhaust steam is used for industrial heating—mention should be made of the generating station at the ANIC Ravenna establishment, which will have an installed capacity of more than 100 MW, equipped with Breda boilers, Tosi turbines and Marelli alternators.

Of gas turbine power plants the more important stations already in service are at Leghorn (two 25 MW units) and at Fiumicino (one 25 MW unit). These are the highest capacity gas turbines installed in Europe. The Martinetto (Turin) power plant, belonging to the Turin Electricity Board, has one 600 kW gas turbine, built by Fiat, running on light petroleum distillates.

Finally, of the power plants equipped with reciprocating engine sets, mention should be made of two already in service: Fiat's Mirafiori (Turin) plant, equipped with four two-stroke diesel engines, with a unit capacity of 15 MW, and Montecatini's Ferrara works, equipped with five 2·5 MW units, running on methane.

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This latter is a particularly outstanding plant as, although of moderate capacity, it has the remarkably high efficiency of 41 per cent; moreover, the exhaust gases are utilized in recovery boilers to produce steam which is used in the nearby factory, and even the engine cooling water is utilized to heat the feedwater of a nearby boiler plant. The overall efficiency achieved in using the heat contained in the fuel is therefore about 62 per cent.

Many of the new power plants are equipped with machinery built in Italy; all the latest have been designed in Italy.

International prize

The 'Mario G. Levi' international prize for the advancement of chemical technology of fuel has been awarded by the Società Chimica Italiana to Professor CARLO PADOVANI, director of Stazione Sperimentale per i Combustibili at Milan, Italy. This prize has been instituted in memory of the late Professor LEVI, director of the Institute of Industrial Chemistry of the Politecnico, Milan, a pioneer of chemical technology of fuel in Italy.

The prize will be assigned every four years, on the occasion of the national congress of the Società Chimica Italiana.

NEW ZEALAND

Information obtained from the Mines Department of New Zealand through the courtesy of the Acting Under Secretary gives the following data for the output of various classes of coal during the year 1957:

	Anthracite	*Bituminous*	*Sub-bituminous*	*Lignite*	*Total*
Underground	1536	811766	1011672	50067	1875041
Opencast	164	18524	590912	127822	737422
	1700	830290	1602584	177889	2612463

The anthracite is a lignite which has been coked by volcanic rock. A large proportion of the bituminous coal is very highly swelling and so worthy of more efficient utilization than is the case at present. The quantities of bituminous, sub-bituminous and lignite mined by the State are as follows: 637646, 948745 and 18133 tons respectively, making a total of 1604524 tons, out of the total output for the country of 2612463 tons.

The 180 MW coal-fired power station at Mercer, sixty miles south of Auckland, is expected to be in operation up to about a third its full capacity in August of this year, with a further 60 MW available at the end of the year. At full capacity this station will require approximately 800000 tons of sub-bituminous coal (of about 10000 B.Th.U.) from the local coalfields. During the next few years most of this will be conveyed by belt from the nearby opencast mine at Maramarua.

Complete gasification of coal

Since it has been pointed out that a quantity of power, equivalent in quantity to that from the Mercer station, could be obtained by the Lurgi high pressure

system from half the quantity of coal with the production costs halved, the Government has shown greater interest and, at its invitation, Dr BRUGGEMANN, formerly of the Gas and Fuel Corporation of Melbourne, has recently visited New Zealand and will report on the possibilities of a Lurgi or other plant for complete gasification and also of a coal-based chemical industry. The most suitable site for such a plant would be in the Waikato coalfield to supply gas to Auckland in the north and to the growing city of Hamilton to the south. In view of the dwindling markets for the west coast coals, new uses for these are needed which will utilize more efficiently their special properties such as high swelling value, tar yield, sulphur and low ash. The Buller coals with almost 50 million tons of coal of high calorific value available to opencast recovery (by normal mining methods giving over 50 per cent slack) could, it is believed, be used efficiently and as an economic proposition for the production of nitrogenous fertilizers for which there is a large potential market in New Zealand.

Following investigations by Professor S. R. SIEMON and Dr T. HAGYARD at Canterbury University, a calcium carbide industry has been suggested for the Greymouth coalfield. A large cement works is about to commence operations a few miles south of Westport. This will use slack from the Buller coalfield.

Utilization of iron sands

Much publicity has been given recently to the development of an iron and steel industry using the iron sands of which there are probably more than one thousand million tons along the coasts of the two islands of New Zealand. Two proposals for starting an industry have been put forward, one by the N.Z. Development Corporation Ltd, the other by American interests supported by Fletcher Holdings Ltd. The Government has set up a committee to report on the desirability and possibility of establishing such an industry in New Zealand. Both groups propose to use Taraniki iron sand (titanomagnetite) containing approximately 60 per cent iron and about 8 per cent titanium. In each case Dunedin is mentioned as a possible site for the works. Boring operations are now being carried out on the proposed site near the entrance to the Port of Otago. A lignite from Benhar, 50 miles southwest of Dunedin, will be used to make the char of which probably 500 000 tons per annum would be required. It is agreed that there is scope for only one large concern.

Coal utilization

In 1957 the railways took approximately 300 000 tons, most of which came from the west coast. With the purchase of more diesel locomotives and the use of oil-fired locomotives in the North Island, greater quantities of oil are being used at the expense of coal. The consumption of diesel oil was 3·5 million gallons and of fuel oil 18 million gallons, together being the equivalent in calorific value of 120 000 tons of west coast coal. There is urgent need for the appointment of a commission to consider the future of the coal industry in particular in relation to the efficient utilization of coal for the production of gas, electricity and chemicals.

Production of oil and natural gas
Drilling for oil has been continued in several areas. Production in the Taranaki district has amounted in 1957 to 205 210 gallons with 6 781 000 ft³ of gas.

Nuclear Science Institute
The Government has recently announced its intention to establish a Nuclear Science Institute within the framework of the D.S.I.R. The University of New Zealand will not only share in the administration of the Institute but its members will also have an opportunity to work in it.

Power from thermal areas
The first 6·5 MW generator at Wairakei is expected to be in operation by the end of September and the second, third and fourth generators early in 1959. By mid-1959 the total output from this station should be 69 MW.

Publications

CHAMBERS'S TECHNICAL DICTIONARY

Third revised edition with supplement. Edinburgh: W. & R. Chambers, 1958. 1028 *pp.* 35*s*

THIS publication is a revised and up-to-date edition of the well-known *Technical Dictionary*. Its main use is for the non-technical person confronted with specialized terms and nomenclature, in particular for the secretary of the technical man. It is also valuable to scientists and engineers whose work takes them into unfamiliar fields.

The main part of the text appears to be virtually identical with the second edition, but the former supplement and addenda have been combined into an enlarged supplement, which includes many of the terms introduced as a result of the rapid development of many branches of science and engineering. The provision of a supplement is a less expensive method of revision than the insertion of the entries at the appropriate alphabetical point, but it is less convenient for the user.

There are a number of minor criticisms which can be made as a result of a series of spot checks. Omissions include the common forms of packings for absorption and distillation columns, the piezometer ring, the slug as a unit of mass, ICA as a petroleum additive, and bumping as a term applied to boiling liquids. The American term 'Freon' is given for fluorinated derivatives of methane and ethane, but the English term 'Arcton' does not appear. Some of the definitions are not very helpful; for instance, fluidization is described as 'The handling of solids (e.g. grains or powders) as if they were liquids'.

In a work of this type, all the technical terms used in a definition should be included as entries in the dictionary. This is not always done; for instance, 'Irish moss' is reported to contain 'fucose', but fucose does not appear in the alphabetical list. Finally, the list of principal contributors is out-of-date, many of those concerned having left their listed posts years ago.

J. F. RICHARDSON

CHEMICAL ENGINEERING PRACTICE
Volume IV Fluid State

Edited by H. W. CREMER and T. DAVIES. London: Butterworths Scientific Publications, 1957. *vi* + 644 *pp.* (*illus.*) 95*s*. U.S.A. edition published in New York by Academic Press Inc. $13.30

IT is not possible to do justice to a work of over 600 pages in a short review, but a number of of features clearly stand out in the fourth volume of this series. It is readily divided into three sections: thermodynamics and introductory fluid flow by R. F. STRICKLAND-CONSTABLE; fluid dynamics by N. L. FRANKLIN and F. H. CASS; and the measurement of process variables by A. POLLARD and T. G. CARRUTHERS.

The treatment of thermodynamics is well tailored to the needs of the chemical engineer, especially in so far as it relates to systems in which no chemical reaction is occurring. Particularly clear are the accounts of the reduced equations of state and the properties of mixtures, and these form a sound basis for the understanding of such separation processes as distillation and extraction; it would have been helpful, however, if numerical examples had been given to enable a comparison to be made of the different methods of calculation. It is a pity that right-angled triangular diagrams are not discussed in relation to the representation of 3-component mixtures as they have the great practical advantage that they can be drawn on ordinary squared paper. The final chapter of the section on fluid flow could profitably have been transferred to the following section. Although molar quantities are

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particularly suitable in physical chemistry, their use in fluid flow gives rise to rather complex equations because the units of force and energy are related to unit mass rather than to unit molar quantity of material. Further, with many of the fluids used in the chemical industry, the molecular weight may not be accurately known.

In the second section, the authors have given a reasonably comprehensive treatment of fluid dynamics, but have made few concessions to the main needs of chemical engineers or to the general title of the series. This has largely arisen from the desire to generalize and to regard the simple cases, Poiseuille's law for example, as particular instances. For that reason, the approach is more suitable for the specialist in fluid dynamics than for the average chemical engineer. Thus pipe friction, whose calculation is probably the most important single aspect of the subject for the chemical engineer, is hastily disposed of with little discussion of such practical topics as pipe roughness, and without the provision of a chart to enable the estimation of flow from the pressure drop over a known length of pipe. Under the heading of compressible flow is included much material which has already appeared in the first section, with the complication that different symbols are employed and no table of symbols is included. The discussion of frictionless flow in a pipe does not seem particularly useful.

The final section which deals with the measurement of pressure, flow rate and temperature, is unfortunately seriously marred by the use of equations which are not dimensionally consistent because of the failure to distinguish between mass and weight. When Bernoulli's equation—which does not receive a mention in the index—appears, it has yet another set of symbols which again are not tabulated.

The general impression of the volume is similar to that of earlier ones. It contains much very good material, but there is little evidence of editing or of contact between the various authors at any stage. The inclusion of a table of symbols with every section and some attempt at standardization would add greatly to the value of the work. The index is not adequate and a spot check revealed a number of serious omissions. The standard of production is good and, although a few errors were spotted, proof reading appeared to have been satisfactory.

J. F. RICHARDSON

HENRY EDWARD ARMSTRONG 1848-1937

J. VARGAS EYRE. London: Butterworths Scientific Publications, 1958. *xix* + 325 *pp.* 30*s*

PROFESSOR ARMSTRONG was a dominant personality in British chemistry and in scientific and engineering education from about 1880 until his retirement in 1912, and was active for twenty five more years as a writer, commentator and internationally known scientific figure. His biography is thus part of the history of the formative period of chemical industry in Britain, and of the development of education for the new technologies. Armstrong's wide-ranging interests, vigour of mind, and intensity of purpose emerge clearly from these pages. So do the individualism and the combative character which occasionally caused him to deviate into unreasonable criticism and intolerance, as in his obstinate opposition to the theory of ionic dissociation in aqueous solution. Such aberrations are small things when set against his contributions to chemical science, his services to the Chemical Society and the British Association, and the educational achievement of his thirty years as Professor of Chemistry at the City and Guilds College in Kensington. When this college became part of the new Imperial College of Science and Technology, and his department was closed, Armstong's academic career ended; but his influence on technical education has survived through the adoption of many of his novel ideas and methods.

The book is a very readable account of Armstrong's life and work, and its relation to the scientific, educational and industrial environment of his day. It also gives a most interesting picture of his personal character and traits, including the endearing foible of wearing multi-hued waistcoats, brilliantly dyed to illustrate the relation between colour and chemical structure. Perhaps more space could have been given in the main text to Armstrong's chemical ideas and discoveries and his stimulating and entertaining controversial writings; sometimes, too, the author's comments have an air of rather uncritical piety, but he has drawn a convincing portrait of a remarkable man.

K. E. WEALE

SCHLACKENKUNDE

W. GUMZ, H. KIRSCH and M. T. MACKOWSKY. Berlin: Springer-Verlag, 1958. *xi* + 422 *pp.* (167 illus.) *DM* 48.00

THE scope of this work is wider than its title suggests since it deals, in fact, not with slags only but with all the forms in which the mineral matter of coal may reappear after combustion in the boiler, whether as slags, fly-ash or deposits. It presents the boiler engineer with a convenient survey of the rather scattered literature and a summarized description of the laboratory techniques which are available for studying his problems and it is therefore the first work of its kind to appear. Because of the breadth of the subject the treatment is necessarily concise, and frequent reference to the original literature will be necessary, but the authors' development is clear and logical and one becomes familiar with the arrangement of the book very quickly.

The first five chapters (143 pages) are devoted to an account of the genesis of the mineral constituents of coal, their nature and significance in boiler practice, and the analytical and mineralogical methods which are used in their estimation and characterization. In the next four chapters (114 pages) the theory of deposit formation is developed, beginning with an account of the thermal breakdown of the minerals themselves and the mineralogy and petrography of slags and deposits, and concluding with a satisfactorily full presentation of the various theories of the mechanism of boiler fouling: the authors' discussion of the physics of deposition of particles on a tube illustrates the complexity of the problem very clearly. The remainder of the book (95 pages) is given principally to a discussion of the practical methods of combating boiler fouling and partly to an account of the utilization of the residues: pulverized fuel, stoker-fired and oil-fired installations all receive attention. Methods of inorganic elementary analysis and a glossary of mineralogical and technological terms are given in appendices (54 pages).

J. D. WATT

SIXTH SYMPOSIUM (INTERNATIONAL) ON COMBUSTION

Published for the Combustion Institute, in New York: Reinhold; in London: Chapman and Hall, 1957. *xxv* + 943 *pp.* $28.00, 224*s*

THIS is another of the now familiar Combustion Symposium books and contains within its 943 pages a vast amount of new information on most aspects of the science of combustion. It is a volume which all serious combustion research workers should have ready access to or, better still, should possess in their personal libraries.

There was no main theme on this occasion, so the technical nature of the Symposium is best indicated by the subject distribution of papers which is as follows: (*1*) structure and propagation of laminar flames—37 papers, (*2*) structure and propagation of turbulent flames—11 papers, (*3*) high speed reactions—8 papers, (*4*) flame stabilization in fast streams —8 papers, (*5*) combustion chamber instability—4 papers, (*6*) ignition—5 papers, (*7*) combustion of explosives and solid propellants—11 papers, (*8*) evaporation and combustion of droplets and sprays—10 papers, (*9*) experimental and analytical techniques in combustion —9 papers, (*10*) applications of combustion—20 papers. In addition three panel discussions on: (*a*) future problems of combustion research, (*b*) high speed reactions and (*c*) flame stabilization in fast streams were reported briefly at the end of the book.

Although the 129 papers presented are generally of a high standard and make definite contributions to the chemical kinetic, aerodynamic and thermodynamic aspects of combustion no outstanding new development is reported, the papers representing advances along previous lines of research. In section (*1*) it is clear that laminar flames are generally well understood from a descriptive viewpoint but theoretically there is need of further work; a clearer understanding and distinction between the physical and chemical factors has been called for by several of the authors who also stressed the importance of chemical kinetics. In section (*2*) the presence of a number of papers on flames involving oxidants other than air reflects the increasing activity in the field of rocket propulsion. Under section (*4*) the purely aerodynamic methods of flame stabilization, i.e. use of high velocity gas and air jets with no bluff body, introduces new interesting possibilities. Section (*8*) shows considerable

progress in the understanding of the behaviour of fuel drops burning under a variety of conditions. Section (*9*) is relatively small but includes a comprehensive survey on the measurement of gas stream temperatures; the reviewer believes that the subject of experimental and analytical techniques in combustion might be taken as a main theme for some future Combustion Symposium and that its growth is the key to a deeper understanding of many of the inner mysteries of flames. Section (*10*) includes papers relating to spark ignition engines, gas turbines and rocket motors as well as four interesting laboratory studies on fire extinction.

The three panel discussions merit close study, particularly (*a*) which was the widest in scope. There was general agreement that future combustion research should be directed particularly to studies of: detonation; high temperature chemical kinetics; flame propagation in homogeneous and heterogeneous, laminar and turbulent systems; combustion instability and rocket combustion. To these topics we may add, in Dr J. S. CLARKE's words, the correlation of the extensive data reported at this Sixth Combustion Symposium.

B. P. MULLINS

PHYSICAL AND AZEOTROPIC DATA
Hydrocarbons and sulphur compounds boiling below 200°C

Edited by G. CLAXTON. London: National Benzole and Allied Products Association, 1958. *vi* + 146 *pp.* 42*s*

REFERENCE books presenting physical data are usually of two sorts. On the one hand there are the encylopaedic types which require reinforced library shelves and a great deal of physical effort each time they are consulted, on the other hand there are the small specialist handbooks which can be kept on the corner of the desk or slipped in a brief case. The book under review is of the latter type and contains a mine of critically selected information in a readily extractable form.

The book is intended as a companion volume to *Motor Benzole, its Production and Use* from the same publishers, a new edition of which is to appear shortly. The greater part of the book is occupied by tabulated data on the melting point, normal boiling point and refractive index (usually at 20°C) of pure hydrocarbons whose normal boiling points lie in the temperature range below 200°C. The coverage is extensive and all hydrocarbons are included for which at least two of the tabulated properties are available. The accuracy of the data is indicated. Similar information is also included for about 160 sulphur compounds in the same boiling range.

The second main subject of the book is a compilation of azeotropic data. The material given represents a checked and extended version of the azeotropic data given by HORSLEY. Approximately 1 400 binary mixtures are listed consisting of both azeotropic and non-azeotropic systems. A smaller number of ternary and quarternary azeotropes is also included. For each system the boiling point and composition of the azeotrope is given together with a full literature reference.

An introductory section of the book describes fully and lucidly the method of classification adopted and also includes a glossary of customary names of the more important benzole components together with the systematic name adopted in the text.

G. G. HASELDEN

Letters to the Editor

Letters to the Editor on points of scientific interest related to fuel science are invited. The Editor does not hold himself responsible for opinions expressed in correspondence. Anonymous contributions cannot be accepted.

Dimension of Side Chains in Coal Structure

A MAJOR part of carbon in coal is believed to be 'ordered', i.e. present in aromatic cluster units, and the other or 'disordered' part is present around the periphery of the structural unit in the form of methyl or methylene groups as indicated by i.r. studies[1]. However, the disposition and, in particular, the dimensions of such side chains (aliphatic and/or alicyclic) are not known. A. WHITAKER[2] recently advanced the view that such chains might be very short and randomly dispersed around the structural unit of coal.

Such a model for the peripheral structure cannot apparently account for the results of oxidation. The mechanism of oxidation of coal advanced[3,4], however, enables some deductions to be made regarding the 'disordered' carbon. The low temperature oxidation of coal in air at 170°C occurs mainly at the end-groups leading to the formation of hydroxyl, carbonyl and carboxyl groups and the aromatic skeleton appears to remain largely unaffected[3]. The most important effect of the oxidation appears to be the formation of

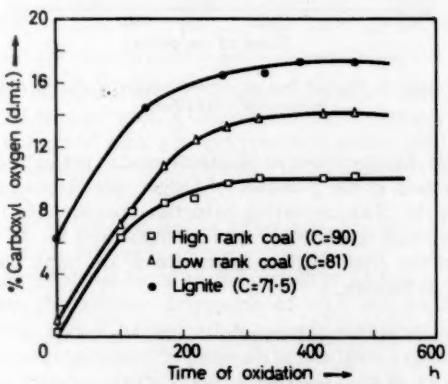

Figure 1. Changes in 'COOH'-oxygen during low temperature oxidation (170°C)

carboxylic groups (*Figure 1*), which can be accounted for only in terms of oxidation of 'disordered' carbon. This fact in conjunction with the material balance data for the coals studied (*Figure 2*) may throw some light on the disposition and dimension of the side chains.

Figures 1 and *2* indicate that the material loss nearly corresponds to the formation of COOH groups until both the values are stabilized apparently

with the complete oxidation of side chains. As the formation of phenolic —OH and quinonoid oxygen[3] leads to some gain in weight in the oxidized coal the loss can reasonably be attributed to the oxidation of side chains (aliphatic and/or alicyclic).

If all the side chains were short aliphatic chains (like methyl, ethyl or propyl) or were made up of short alicyclic networks, then on complete oxidation there would have been an overall gain in weight in either case.

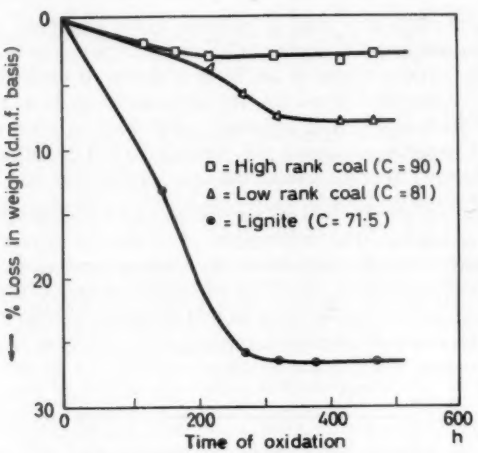

Figure 2. Overall loss of organic material during low temperature oxidation

Such a disposition has therefore to be discounted in the light of experimental data. An assumption of the presence of longer side chains appears to be in conformity with the changes during oxidation, particularly if such changes are viewed in relation to D. W. VAN KREVELEN and H. A. G. CHERMIN'S[5] structural model for coal. Such a model for a low rank coal[3] (C = 80·7 per cent) may be as follows:

$$C\ \% = 80{\cdot}7,\ \text{Unit weight} = 394,\ \text{No. of rings} = 5$$

$$R/C = 0{\cdot}23,\ H/C(\text{corrected}) = 0{\cdot}817,\ O/C = 0{\cdot}112,\ f_a = 0{\cdot}71$$

The aromaticity[4, 5], f_a, of such a coal being known (0·71) the 'ordered' and 'disordered' carbon in the model is calculated to be as follows:

$$\text{Aromatic carbon} = 19,\ \text{Disordered or Non-aromatic carbon} = 8$$

The carboxylic oxygen content of the 'final' oxidized product of such a model is of the order of 14 to 16 per cent (*Figure 1*) and final loss in weight in the process is of the order of 8 per cent (*Figure 2*).

The eight non-aromatic carbon atoms at the periphery of the given model may exist in three possible dispositions: (*1*) aliphatic chains, (*2*) alicyclic networks, and (*3*) partly alicyclic and partly aliphatic chains.

In the first case, the eight 'disordered' carbon atoms available for the particular model may be distributed in a single long chain or in a number of smaller chains. But an analysis of the different arrangements indicates that only an average dimension of at least four-carbon-system chains can account for the loss in weight as well as the percentage of carboxylic groups obtained.

With regard to the second case where the 'disordered' carbon is assumed to be present in alicyclic networks alone, only a single network consisting of all the available eight carbon atoms is consistent with the oxidation data. The assumption of two or more networks out of this eight carbon atoms is untenable, as these would have led to a considerable gain in weight along with an unusually high and improbable percentage of carboxylic groups.

Table 1. Air oxidation at 170°C of an anthracite sample (C = 93·2)
(Data on unit coal)

Time of oxidation h	*% wt increase*	C	H	N + O	'OH'	CO	COOH
0	—	93·2	3·5	3·3	*Nil*	*Nil*	*Nil*
200	1·9	90·2	2·7	7·1	1·8	1·5	0·6
400	3·0	89·5	2·6	7·9	2·0	2·0	0·7
600	4·0	88·7	2·7	8·6	2·1	2·2	1·9
800	3·9	88·1	2·5	9·4	2·1	2·3	2·1
1000	4·0	88·1	2·6	9·3	2·1	2·4	2·1

Regarding the third possibility, i.e. a mixed aliphatic-cum-alicyclic structure of the disordered carbon, such a combination also appears to be ruled out because the oxidation of such a mixed structure should lead to much higher carboxylic content and the loss in weight (experimental) does not support such a hypothesis.

It may therefore be inferred that in general the 'disordered' carbon in coal structure (at least for the range of coals studied, C = 71·5 to C = 90·3) is present in either aliphatic or alicyclic networks and not in combinations of both. Further the average dimension of such side chains, if aliphatic, cannot be less that that of a four-carbon-system, and if alicyclic, the average length of such networks cannot be made up of less than 7-carbon systems.

Such a hypothesis appears to be borne out by a study of the oxidation of an anthracite sample. In view of its high aromaticity and the probable occurrence of shorter chains, anthracite is expected to show gain in weight on oxidation, and is found to do so (*Table 1* and *Figure 3*).

The oxidation at 170°C was continued for 1 000 h and the gain in weight cannot apparently be explained in terms of the so-called 'coal-oxygen-complex'[6] which is known to be unstable above 70°C.

The inference drawn about the probable dimension of alkyl chains in coal structure from coal oxidation studies also appears to be supported by

the recent work of R. S. MONTGOMERY *et al.*[7] on the nature of benzene polycarboxylic acid obtained on drastic oxidation.

It must, however, be pointed out that the inferences about the alkyl chains relate to overall samples of coal and not to vitrains or any other maceral. Further work, since the preparation of this note, indicates that the

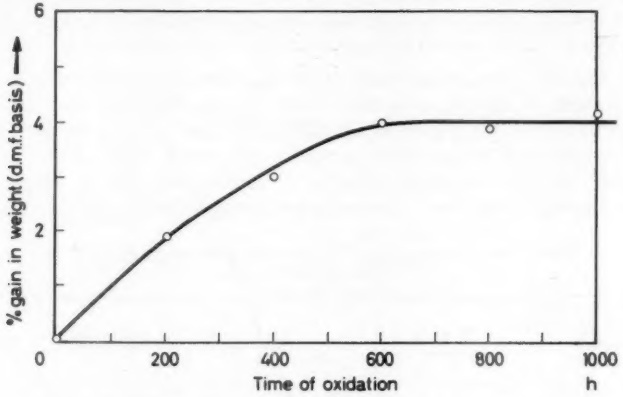

Figure 3. Overall gain in weight during low temperature oxidation (170°C) of an anthracite

concept of bigger side chains in coal structure may have to be modified at least in the case of high rank vitrains (C>85).

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Disposition of Hydrogen in Coal Structure

THE mechanism of oxidation of coal[1] recently advanced leads to a direct approach for the determination of aromatic and aliphatic (and/or alicyclic) hydrogen in coal and broadly supports the different forms of hydrogen in coal as shown by i.r. studies[2]. Earlier, it was shown how the aromaticity of

coals (fraction of carbon in aromatic form)[3] could be determined from oxidation studies. In low temperature oxidation of coal in air at 170°C, the aromatic skeleton of coal remains unaffected and oxidation appears to be selectively restricted to the end groups of coal structure, leading to the formation of additional functional oxygen groups such as COOH, OH and CO. Computation of both aromatic carbon and hydrogen from the 'final' oxidized product of coal is possible provided the oxidation of disordered carbon is complete. That such a stage is attained in oxidation is indicated from the immunity of the sample to further oxidation[1, 3] after a time.

It appears that all the aromatic hydrogen originally present in the coal is retained in the 'final' oxidized product, except for that which has undergone either conversion to additional phenolic —OH groups or is replaced by the formation of quinone groups. Obviously, a correction for the amount of hydrogen replaced by quinone groups is necessary for the calculation of total aromatic hydrogen of the coal. (For this, all the carbonyl oxygen formed in the course of oxidation is assumed to be in quinonoid form as indicated by i.r. studies[4]). Also, another correction is required for the residual non-aromatic hydrogen associated with carboxylic groups.

Table 1. Chemical composition and oxygen groups of original and oxidized coal

Coal No.	Original coal				'Final' oxidized product					Material loss or gain by oxidation
	C %	H %	H/C	f_a*	C %	H %	Functional oxygen, per cent			
							COOH	OH	CO	
1	71·53	4·66	0·79	0·56	61·50	2·38	17·5	7·3	3·0	−26·6
2	80·69	5·33	0·79	0·71	67·80	2·10	14·3	2·3	4·0	−8·0
3	85·15	5·70	0·80	0·69	67·20	2·38	14·3	4·0	3·0	−5·0
4	90·31	4·86	0·65	0·77	76·00	2·40	10·3	3·0	3·7	−2·9
5	93·24	3·52	0·45	0·97	88·08	2·59	2·1	2·1	2·9	+4·2

* Calculated from oxidation studies.

Table 2. Calculation of different forms of hydrogen

Coal No.	Calculation based on oxidation of 100 g of coal substance						$\frac{H_{ar}}{C}$	$\frac{H_{al}}{C}$	$\frac{H_{ar}}{H}$
	H		Corrections for		Total aromatic H per 100 g coal substance	Total non-aromatic H per 100 g coal substance			
	orig. g	oxid. g	H (aliphatic)* g	H (aromatic)† g					
1	4·66	1·75	−0·40	Nil‡	1·35	3·31	0·23	0·56	0·29
2	5·33	1·93	−0·41	+0·13	1·65	3·68	0·25	0·54	0·31
3	5·70	2·26	−0·42	+0·16	2·00	3·70	0·28	0·52	0·35
4	4·86	2·33	−0·31	+0·21	2·23	2·63	0·30	0·35	0·46
5	3·52	2·70	−0·09	+0·19	2·80	0·72	0·36	0·09	0·79

* H corresponding to COOH groups.
‡ Aromatic H replaced by quinone groups.
† In case of the lignite sample no extra quinone groups were formed and hence no correction.

The relevant data and the method of calculation of aromatic hydrogen on the above principle are presented in *Tables 1* and *2*.

In *Table 2*, in addition to the values of total aromatic hydrogen thus obtained from oxidation studies for the different ranks of coal, atomic ratios such as H_{ar}/C, H_{al}/C and H_{ar}/H have also been presented. It will be found that aromaticity of hydrogen, H_{ar}/H, progressively increases with increasing coalification (C = 71 to 94 per cent) and appears to be consistent with those

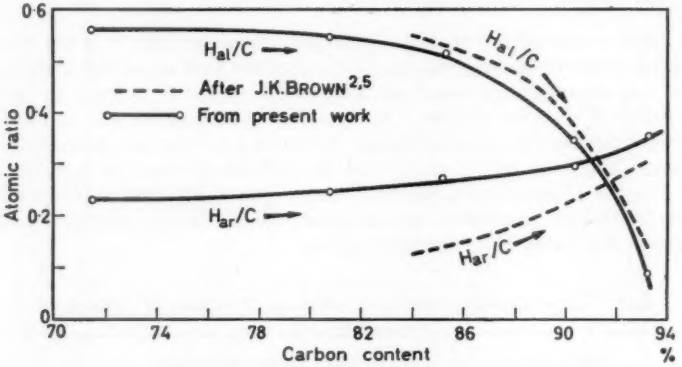

Figure 1. Variation of atomic ratios, H_{ar}/C, H_{al}/C, *with rank of coal*

found by J. K. BROWN and P. B. HIRSCH[2] from i.r. studies. Further, the atomic ratios, H_{ar}/C and H_{al}/C, obtained experimentally, when superimposed on Brown's curve[2] (*Figure 1*) indicate an agreement, particularly for the non-aromatic line. Though the nature of the two sets of curves is similar, the values of atomic ratios are not in quantitative agreement. The discrepancy may be due to the fact that Brown's work was based on vitrain

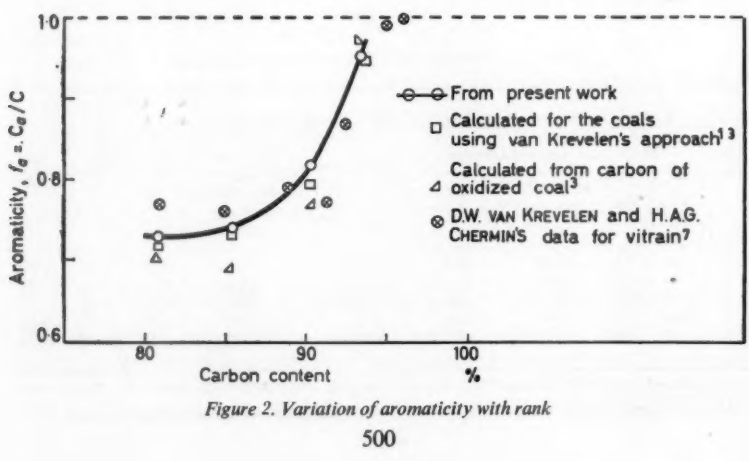

Figure 2. Variation of aromaticity with rank

samples, whereas the present work relates to average coal samples. It may also be due to difficulties in accurate measurement of the optical densities[5], particularly for the lower rank coals. Be that as it may, it is interesting to note the good agreement between the two sets of estimates obtained from completely different premises.

Again, further support appears to be lent to the determined values of H_{ar}/C and H_{al}/C by a calculation of aromaticity of carbon in coal direct from aliphatic or non-aromatic hydrogen. Assuming that the amount of aliphatic carbon is approximately half of that of aliphatic hydrogen (the validity of such an assumption appears to be borne out from the recent concept of longer side chains in coal structure[6]), the fraction of aromatic carbon (f_a) can be calculated. The results are shown in *Figure 2*. The aromaticity, thus calculated directly from determined aliphatic hydrogen, is not only in good agreement with values obtained earlier directly from carbon[3], but also with those given by D. W. VAN KREVELEN and H. A. G. CHERMIN[7].

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The Contact Angle of Mercury at Coal and Char Surfaces

A SHORT communication by S. KRUYER and D. W. VAN KREVELEN[1] on the contact angle of mercury at coal and char surfaces has attempted to explain the marked differences between the values assumed by L. C. DRAKE and H. L. RITTER[2], P. ZWIETERING and D. W. VAN KREVELEN[3], and those observed experimentally by O. G. INGLES[4].

Kruyer and van Krevelen suggest that calculation of the experimental data of Ingles involves an assumption that all pores in his experimental plugs have uniform radius *r*. In fact, no such assumption is made, as is clear from the experimental technique of the wetting pressure method of measurement. In this method the pressure at which mercury first penetrates the plug is noted (this will correspond to penetration of the few largest pores at their narrowest constrictions) and, for the same plug, with one end in contact with the appropriate wetting liquid and the other end with air, the

pressure at which bubbling just commences at the liquid end is noted (corresponding to penetration of the wetting fluid in the few largest pores at their narrowest constrictions, since air will already have been displaced from the finer pores by capillarity).

Provided complete wall contact occurs, the above method is strictly valid and is totally independent of the model adopted, since no structural parameter appears in the derived equation for cos θ, viz.

$$\cos\theta = P_1\gamma_2/P_2\gamma_1$$

where P_1 and P_2 are the experimentally measured pressures and γ_1 and γ_2 are the fluid surface tensions.

Where incomplete wall contact occurs, however, the simple equation $P = (C/A)\gamma\cos\theta$ (where C = perimeter of pore, A = area of cross section of pore) must be replaced by the equation $P = (\gamma C_1\cos\theta + \gamma C_2)/A_1$ where C_1 is the wetted pore perimeter, C_2 the non-wetting perimeter and A_1 the cross sectional area of the liquid (J. BARKER and O. G. INGLES[5]). Using the latter relationship, the mercury penetration pressure P_1 is given by:

$$P_1 = \gamma_1(C_1\cos\theta + C_2)/A_1 \equiv 2\gamma_1\cos\theta/r_e'$$

where r_e' is the equivalent radius for a cylindrical pore model.

The penetration pressure of air against the reference wetting fluid is similarly given by

$$P_2 = \gamma_2(C_1 + C_2)/A_2 \equiv 2\gamma_2/r_e$$

where r_e is the appropriate equivalent radius. Combination of the two equations yields the general relationship for cos θ, viz.

$$\cos\theta = \frac{P_1\gamma_2}{P_2\gamma_1} \times \frac{r_e'}{r_e}$$

This equivalent radius factor which enters the equation for cases of incomplete wall contact can be evaluated geometrically for the case of close packed spheres. In the extreme case of complete wetting and complete non-wetting liquids, the factor r_e'/r_e is then found to be numerically equal to $(3/\pi)[(2\sqrt{3} - \pi)/(2\sqrt{3} - 3)] = 0{\cdot}66$.

The criterion for complete wetting and displacement in any irregularly shaped pore can be shown readily to be that $\theta \leqslant \frac{1}{2}(\pi + \alpha)$, where θ is the contact angle, and α the smallest acute angle in the pore cross section.

It is of interest to note that contact angles for mercury (with other than carbonaceous materials) lower than those originally suggested by Drake and Ritter have been indicated by the work of E. P. BARRETT, L. G. JOYNER and R. SKOLD[6], C. N. COCHRANE and L. A. COSGROVE[7] and others.

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X-Ray Scattering Intensities of Anthraxylons Reduced with Lithium in Ethylenediamine

L. REGGEL *et al.*[1] have shown that lithium in ethylenediamine is a powerful reducing agent for aromatic rings and olefinic and carbonyl linkages; moreover, cleavage of C—C bonds does not occur. The system has also proved to be very effective in hydrogenating coals as judged from the ultimate analysis and the i.r. spectra of the reduced samples[2].

To determine the effect of this reduction on the carbon skeleton of coal, an X-ray investigation of reduced coals was undertaken. Examination of scattered X-ray intensities revealed that extensive changes had indeed occurred in the arrangement of carbon atoms as a result of reduction. This report gives the results of preliminary analyses of scattered X-ray intensities.

The most apparent major change was in the (002) reflections, the most prominent part of anthraxylon patterns. At first glance at the intensity curves, one might presume that a new band has appeared in the angular range corresponding to spacings of 4 to 5 Å, in place of the (002) band at 3·6 Å. The exact position of the new peak depended upon the degree of hydrogenation. The low-angle scattering intensities of two reduced anthraxylons and an untreated sample are shown in *Figure 1*. The curve of the untreated sample (a) is similar to that of a sample treated with the amide $H_2NCH_2CH_2NHLi$ in ethylenediamine (not shown). Their peak positions correspond to a layer separation of 3·6 Å. The sample moderately reduced (b) has a peak position at 4·3 Å, the sample reduced extensively (c) at 4·8 Å. The hydrogen contents of the reduced samples were 6·33 and 7·11 per cent, respectively, as compared with 5·24 per cent for the untreated sample. In the plot shown, the intensity curves of the reduced samples appear as displaced (002) peaks. Whether they are displacements or new peaks, their positions vary greatly with the degree of hydrogenation and may offer a quantitative means of following the course of the reduction. An authentic interpretation of the changes in the patterns may be possible after profile analyses and cosine transforms[3] of these curves have been obtained.

Profile analyses of the (002) band of anthraxylons have shown that this band arises from the parallel packing of planar aromatic ring clusters. For Pittsburgh anthraxylon the average number of rings in the clusters lies[4] between 1 and 3. About 50 per cent of the layers have no specific orientation with respect to each other, i.e. they occur singly; the remainder occur largely

in groups of two parallel layers separated by 3·6 Å. In the light of this information, the change in the intensity patterns as a result of reduction can be considered mainly a displacement of the (002) band assuming that carbon atoms in the hydrogenated layers are now slightly displaced from the planar positions forming buckled layers. The amount of hydrogen added to the layers influences the distance of their separation. These considerations appear reasonable in the light of the enhanced broadness of the displaced peaks (not very apparent from *Figure 1*).

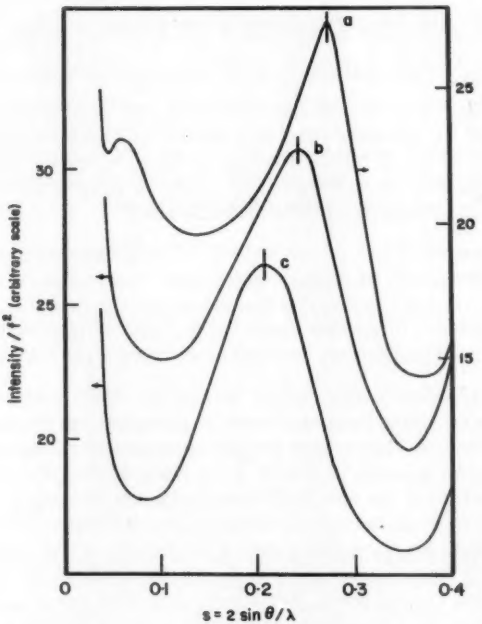

Figure 1. Low-angle scattering of Pittsburgh anthraxylon (a) *untreated,* (b) *moderately reduced, and* (c) *strongly reduced with lithium in ethylenediamine*

Scattered intensities in the angular region where the (11) reflections of aromatic ring clusters occur are shown in *Figure 2*. A quantitative study of the line profiles showed extensive changes in the line shapes as well as peak positions. The line profile of the strongly reduced sample can no longer be explained on the basis of planar aromatic molecules[5–6]. The curves shown might arise from saturated alicyclic layers provided there is an ordered but not excessive buckling[7]. The ripples to the right of the peak may be caused by buckled structure. Calculation of average C—C bond length showed an increase of about 5 per cent for this highly reduced sample, i.e. from 1·395 to 1·47 Å. The latter value is obtained by analogy to planar molecules[3] and corresponds to projected bond length on a plane parallel to the buckled

layers. These results are only compatible with hydrogenation of aromatic nuclei.

The profile analysis of the sample treated with amide in ethylenediamine (not shown) indicated that the treatment brought about some changes in the

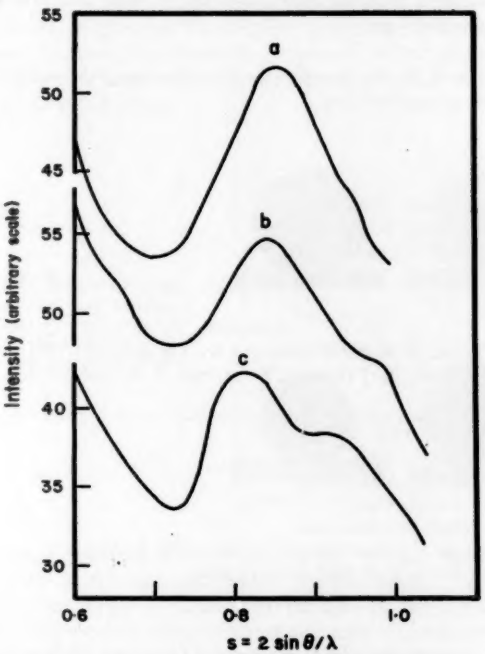

Figure 2. High-angle scattering of Pittsburgh anthraxylon (a) *untreated,* (b) *moderately reduced, and* (c) *strongly reduced with lithium in ethylenediamine*

arrangement of carbon atoms, the major change being an increase in the fraction of carbon atoms that are roentgenamorphous as far as the (11) reflections are concerned. This could be caused by the strain brought about by some slight dehydrogenation that the amine solvent could cause[8] and by the introduction and removal of the amine solvent. It might be interesting to compare this effect with the effect of sorption of vapours that swell coals. The profile of this band is very sensitive to changes caused by strain, buckling, etc.

The present study included anthraxylons having carbon contents from 78 to 89 per cent. X-Ray diagrams showed that the aromatic nuclei in each case were hydrogenated.

The above results suggest that the γ band observed with yellow translucent humic matter (spores, cuticles, etc.)[9] in coals could arise from parallel

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alicyclic layers. However, the yellow matter should be studied for possible aliphatic content.

A thorough study of the high-angle x-ray scattering intensities of the reduced coals will necessarily await some theoretical work on the scattering from partly and completely reduced aromatic molecules. A complete analysis of the (002) bands of reduced coals, differing in rank and in degree of reduction, will be reported later.

We wish to thank R. Raymond of the U.S. Bureau of Mines for supplying the reduced samples of anthraxylon.

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Contact Angle between Mercury and Coal

THE pore size distribution of South African coals[1] has been studied by the method developed by H. L. RITTER and L. C. DRAKE[2] which requires a knowledge of the contact angle between coal and mercury. The contact angle was measured for a number of coals and the average value obtained used in the calculations. Since the variation from one coal of the series investigated to another was not very large the use of an average value did not have an appreciable effect on the results.

O. G. INGLES[3] recently reported values of the contact angle between mercury and coal and chars that differ considerably from the values quoted by us[1]. It appears advisable, therefore, to describe briefly the method used and results obtained in this laboratory.

The method involved photographing the enlarged profile of a small drop of mercury placed near the edge of a flat piece of coal or pellet compressed from powdered coal. Photographs were taken while specimens were either under a vacuum or at atmospheric pressure.

Enlargements were made from the negatives and the required dimensions measured on the prints. The total enlargements of the image of the drops was about 400.

The contact angle was calculated from the dimensions of the drop according to the method devised by G. L. MACK and D. A. LEE[4]. This procedure is more accurate than the direct measurement of the angle because the error in judgement involved in drawing the tangent to the curve of the drop at the point of contact becomes increasingly important as the angle approaches 180°. In *Figure 1* some typical photographs are shown which indicate that the mercury–coal angle is fairly large.

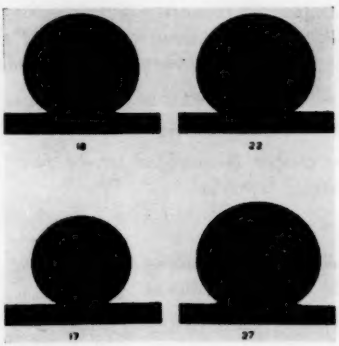

Figure 1. Photographs of small mercury drops on coal surfaces. (The measurements were made on enlargements where the drop diameter was approximately 20cm)

The information required for calculating the contact angle is; (*a*) the radius of the drop at the equator, (*b*) the vertical height, (*c*) the radius of curvature at the apex, and (*d*) the length of the base of the drop. Because (*c*) cannot be measured directly with sufficient accuracy it is calculated from the capillary constant of the liquid as indicated by N. E. DORSEY[5].

As suggested by A. W. PORTER[6], G. L. MACK[4] and G. A. BRADY and A. W. GAUGER[7] small drops have been used in making these measurements. It was found possible to use drops of only 0·5 mm diameter. The contact angles obtained by this method, using such small drops are the 'advancing angle'. The method yields a value which is the integral of the sum of all the separate

Table 1. Contact angles for different types of coal

Coal sample No.	*Proximate analysis*			*Contact angle*
	H_2O %	*Ash* %	*VM* %	
1	1·9	10·0	6·3	147°
2	4·5	22·0	23·4	148°
4	1·0	13·4	23·2	145°
5	1·2	12·6	19·2	140°
6	1·9	10·0	6·3	143°
7	4·5	22·0	23·4	146°

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angles along the contact circumference. This is an advantage when working with a substance with such a variable surface as that of coal.

Measurements made in a vacuum and at atmospheric pressure did not show variation. Increase in pressure would decrease the angle (due to surface porosity) whereas the adsorption of gases would increase it (mercury–air contact angle large). It would appear that these opposing effects balance each other at atmospheric pressure and when evacuating the vessel containing the coal sample to the same extent, and this may account for the fact that the angle was not affected when measured under these two sets of conditions.

The values listed in *Table 1* were obtained from measurements made at atmospheric pressure on dried samples of coal. The proximate analyses of the samples are also given. Samples Nos 7 and 6 refer to pellets made from coal powders obtained from coals No. 2 and No. 1 respectively. The powders (−60 mesh B.S.S.) were pelleted in a hand press.

It will be observed that the variation in contact angle is not very large with the types of coal studied.

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True Density of Cokes from Blends

THOUGH the blending of coals for production of metallurgical coke has long been known, the action of blends is not well understood. It was thought that the true density of cokes from blends might throw light on this problem. Four types of binary blends were used in the investigation: (*i*) a medium volatile Jharia (XII seam) coal (60 per cent) and a high volatile Dishergarh coal (40 per cent), (*ii*) a low volatile Jharia (Zero seam) coal (30 per cent) and a high volatile Dishergarh coal (70 per cent), (*iii*) a high volatile Dishergarh coal (85 per cent) and low temperature char from a low rank Jambad Bowlah coal (15 per cent), and (*iv*) a high volatile Dishergarh coal (90 per cent) and coke breeze from the same coal (10 per cent). These blends had previously been found to give good metallurgical cokes (*Metallurgical Coke from Raniganj Coals*. Fuel Research Institute: Jealgora, Bihar, India, 1955).

The carbonization was effected by heating the samples in a vacuum to 1 000°C at the rate of 5°C/min and maintaining at that temperature for 2 hours. In order to minimize errors due to uncertainty regarding the correction for mineral matter, samples rich in vitrain were used in the present study. The densities were determined in argon and since it was found that the gas was adsorbed at room temperature, measurements were carried out at 218°C, where adsorption did not appreciably vitiate the results. The data are presented in *Table 1*.

Table 1. Densities of cokes from coals and blends

No.	*Coke or char*	*True density g/cm³ d.a.f.**
1	*Jambad Bowlah char*	1·72
2	*Dishergarh coke*	1·80
3	*Jharia (XII seam) coke*	1·74
4	*Jharia (Zero seam) coke*	1·89
5	*Coke from a blend of Jharia (XII seam) coal and Dishergarh coal*	1·85
6	*Coke from a blend of Jharia (Zero seam) coal and Dishergarh coal*	2·01
7	*Coke from a blend of Dishergarh coal and Jambad Bowlah low temperature char*	2·02
8	*Coke from a blend of Dishergarh coal and coke breeze from the same coal*	2·00

* The density of ash has been taken as 2·50 in the calculation.

It is seen that the density of the coke from the blends is higher than the densities of the individual cokes. The blend, in other words, behaves in carbonization as a coal, higher in rank than either of the components. Herein may lie an explanation for the action of blends in coking, although the mechanism by which the density of cokes from the blends increases is not clear at present.

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The Oxygen–Carbon Relationship in Coals

DURING the preparation of the paper published recently[1] on oxygen and hydrogen in coals, two disturbing factors, not then mentioned, came to light which have now been largely resolved. The first was that in the relation

$$[(O + S)/C]^{\frac{1}{2}} = K(100 + k - C) \quad \ldots . [1]$$

where O, S and C are the oxygen, sulphur and carbon percentages by weight, and K and k are two constants; all but the British and (European) Continental

coals gave a line not passing through the origin. Though this does not contradict equation 1 over the experimental range for which it is valid, this intercept is physically meaningless since when C = 100, (O + S) must be zero. It has now been found that the need for the intercept, k, can be removed by using an index slightly greater than $\frac{1}{2}$ on the LH term of equation 1. The corrected equation therefore reads

$$[(O + S)/C]^{1/n} = K(100 - C) \quad \ldots . [2]$$

This replaces the arbitrary intercept constant, k, by an arbitrary index constant, n, so three constants are still required to specify the band namely: the slope, K; the band width, $\pm w$ (see ref. 1); and the index, $1/n$. When tested on the representative data for American coals used for *Figures 1* and *2* in the previous paper[1] (the data being taken from the *International Critical Tables*[2])

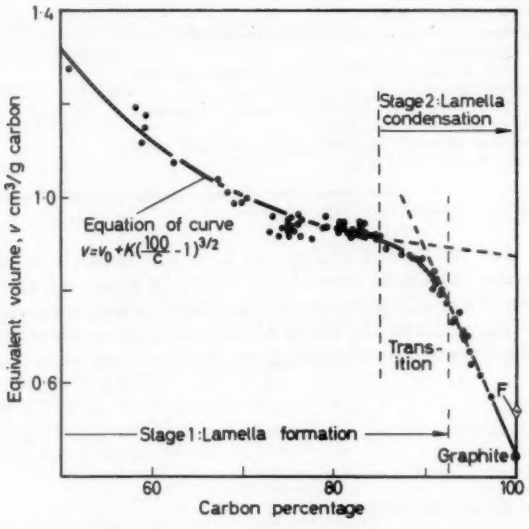

Figure 1. Variation of equivalent volume of coals with their carbon percentage

the new values of n and K were found to be 1·9 and 0·021 compared with the previous values of 2 and 0·0185.

The second point for concern was that, to a first order of magnitude, the experimental points fitted equation 1 over the whole range from 40 to 100 per cent carbon, whereas on the two-stage theory of coal formation[3, 4], based on the Two-Component Hypothesis of coal constitution[5, 6], a break or change in slope of the line was to have been expected at approximately 90 per cent carbon. Such a change can be seen in most plots of coal properties against carbon percentage, for example *Figure 1*, which illustrates the two-stage theory as reported elsewhere[4], shows the variation of equivalent volume

(specific volume/C) against carbon percentage with a transition between the two stages at about 90 per cent carbon. It was true that, in the plots based on equation 1, a slight tendency for the points to deviate from the line could be observed but the data available were insufficient for a significant conclusion to be drawn. However, some recent statistical calculations[7] have now confirmed that there is a slight but significant change above 90 per cent carbon. Furthermore, the log/log plot used to determine the index constant, n, in equation 2 suggests that n may change slightly in value at 90 per cent carbon, although here again the data available are not sufficient for a significant conclusion to be drawn.

In the paper reporting their statistical calculations, J. M. RUCKLIDGE and his co-authors[7] point out that many organic compounds fail to fit the coal band. In the original paper[1], only those fitting the band were selected to avoid confusion on the graph illustrating the relation. The point was also made that the materials selected for plotting were coal derivatives with the implied corrollary that, for those coal derivatives *not* fitting the coal band, the displacement from the band might provide some indication of the alteration produced by the process of derivation.

These writers[7] also suggest that, in spite of the high correlation they found to exist between the quantities $[(O + S)/C]^{\frac{1}{3}}$ and C, equation 1 was nevertheless fictitious; the reason given being that the two variables were not independent! It is of course a reasonable *a priori* assumption that the two variables are chemically interdependent, and in support of this equation 1 shows that they are also mathematically interdependent; so the conclusion that the relationship is fictitious is self-evidently untrue since it is shown[7] that the fit of the experimental points is significant at the 99·9 per cent probability level.

A more valid criticism, which was of course carefully examined before preparation of the original paper[1], would be the charge of triviality, and by inference from associated comments in the letter[7], this is possibly what was intended by the term fictitious. The possibility of triviality stems from the use of percentages when quoting coal analyses (which is a further argument in favour of reverting to the standard practice in normal organic analysis of using ratios by weight or number of atoms). Since

$$C + H + N + O + S = 100 \qquad \ldots . [3]$$

there is a mathematically trivial relationship between (O + S) and C which can be written

$$(O + S)/C = [(100 - C) - (H + N)]/C \qquad \ldots . [4]$$

and for (H + N) small, this can be written (cf. equation 1)

$$[(O + S)/C]^{\frac{1}{3}} \simeq [(100 - C)/C]^{\frac{1}{3}} \qquad \ldots . [5]$$

Obviously with two variables there can only be one equation so—if the condition that (H + N) is small is true—equation 1 must either be trivial or fictitious. Since it has been shown above to be not fictitious it must be either trivial or else (H + N) is not small. If this latter is true then two equations (1 and 4) for three variables is mathematically possible.

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Assuming (H + N) to be small or zero, the mathematical condition for the triviality of equation 1 is that it should be identical with equation 5. This identity can be written

$$K^2 (100 + k - C)^2 \equiv (100 - C)/C \quad \ldots . [6a]$$

which must hold for all values of C. In fact, for British and Continental coals, $k = 0$ and this cubic reduces to a quadratic which has only two solutions, i.e. only two values of C for which equations 1 and 5 have identical values. For these coals, $K = 0{\cdot}020$, and equation 6a is a perfect square which can be written

$$(C - 50)^2 \equiv 0 \quad \ldots . [6b]$$

As this showed that a strict identity did not exist, the possibility of an approximate identity [implying that (H + N) was small rather than zero] was next tested by plotting the LH term of equation 6a against its RH term. For a strict identity (disproved theoretically) a straight line of unit slope would have been obtained; and for the approximate identity the condition was that

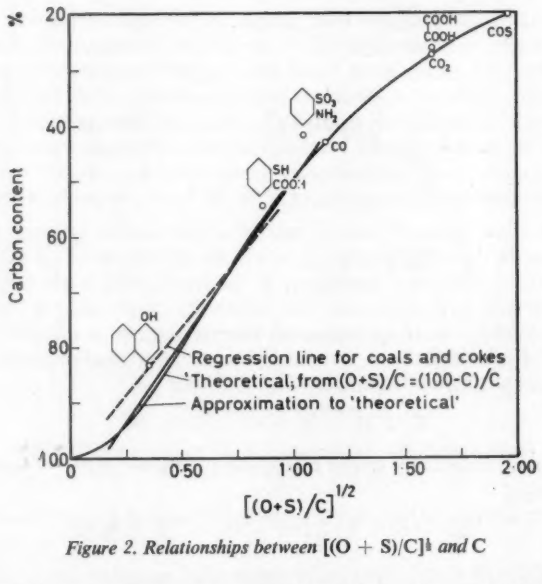

Figure 2. Relationships between $[(O + S)/C]^{\frac{1}{2}}$ *and* C

this line would have to be a good approximation to the actual line obtained. In fact, the line obtained diverged markedly from the unit slope line, just as in *Figure 2* (*Figure 1* of Rucklidge's paper[7]) the calculated regression line diverges both from the 'theoretical', i.e. trivial, line of equation 5 and from the linear approximation thereto.

As this argument indicated that (H + N) was not negligible, it was checked by calculating the displacement from the trivial line that the (H + N) term

could produce on the plot of *Figure 2*. On this plot the percentage displacement (D per cent) in [(O + S)/C][1] for any given value of C can be written, taking only the first term of the expansion,

$$D\% = -50(H + N)/(100 - C)$$

Calculation shows that as C rises from 60 to 95 per cent, the percentage displacement rises from 5 to 30 which, as can be seen from *Figure 2*, is not negligible.

Since this argument for triviality seems to be based upon a misappreciation of the importance of (H + N), which was assumed to have a negligibly small range of values, it is of interest to consider the converse approach and examine the *a priori* predictions to be expected if all three variables had similar ranges of values. As shown above, the displacement from the trivial line of equation 5 depends on the value of (H + N). Mathematically there is no restriction upon the value of (H + N) between the limits 0 and 100 per cent (provided of course that equation 3 is also obeyed), though there may be chemical restrictions. Since the limiting case is obtained when (O + S) is zero this means that *a priori* we could expect to find points lying anywhere between the trivial line and the carbon axis. The restriction of the points to a narrow band, which as has been shown[7] is significantly displaced from the trivial line, is therefore due presumably to some chemical (e.g. valency) restriction. The significance of the restriction is also underlined by the greater scatter, conclusively confirmed[7], that is shown by most organic materials of known formula. If equation 1 was trivial, *all* these organic materials whether coals or not would have to fit the line. The demonstrated scatter confirms that equation 1 cannot therefore be trivial. Also as Rucklidge *et al.*[7] are at pains to point out, this is particularly true of those materials containing sulphur. This is of course entirely to be expected since, in the materials quoted, sulphur cannot be replaced weight for weight by oxygen.

It is concluded therefore that equation 1, and its modification equation 2, is neither fictitious nor trivial; that the charge of its being trivial seems to be based on a misappreciation of the importance of the third variable (H + N); and that, for the same reasons, R. A. MOTT's[8] criticism of H. BRIGGS's[9] linear approximation equations is also invalid.

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I HAVE seen the letter of R. H. ESSENHIGH[1], which purports to answer the criticism of my colleagues, J. M. RUCKLIDGE, W. C. THOMAS and H. C. WILKINSON[2], of his earlier paper[3]. In this he ventures to suggest that my criticism[4] of Briggs's 'development lines' is invalid.

Briggs plotted development lines on axes of carbon and oxygen for, among others, fusain, durain, cannel and torbanite, most of the data being for a range of carbon of 90 to 75, and C + H + O = 100. My criticism of this plot was that, since the hydrogen contents of these materials are at certain well known and different levels and, therefore, for each 'species' the plot was merely of C against 100−C, the straight lines were a mathematical consequence of using dependent variables and were therefore misleading. That criticism stands despite Essenhigh's assertion.

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